



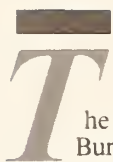
## NBS TECHNICAL NOTE 1207

U.S. DEPARTMENT OF COMMERCE/National Bureau of Standards

# NBS Reactor: Summary of Activities July 1983 Through June 1984



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- Polymers
- Metallurgy
- Reactor Radiation

<sup>1</sup>Headquarters and Laboratories at Gaithersburg, MD, unless otherwise noted; mailing address Gaithersburg, MD 20899.

<sup>2</sup>Some divisions within the center are located at Boulder, CO 80303.

<sup>3</sup>Located at Boulder, CO, with some elements at Gaithersburg, MD.

# NBS Reactor: Summary of Activities July 1983 Through June 1984

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Frederick J. Shorten, Editor

Reactor Radiation Division  
National Measurement Laboratory  
National Bureau of Standards  
Gaithersburg, MD 20899

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*NBS Technical Note*

U.S. DEPARTMENT OF COMMERCE, Malcolm Baldrige, Secretary  
NATIONAL BUREAU OF STANDARDS, Ernest Ambler, Director

Issued February 1985

National Bureau of Standards Technical Note 1207  
Natl. Bur. Stand. (U.S.), Tech. Note 1207, 161 pages (Feb. 1985)  
CODEN: NBTNAE

U.S. Government Printing Office  
Washington: 1985

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For sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402



## FOREWORD

The National Bureau of Standards Reactor was built not only to serve the needs of the NBS but also those of other government agencies as a National Center for the application of neutron methods to problems of national interest. The Reactor Radiation Division was established to operate the reactor and to foster its scientific and technological use. Toward this end, the Division has a small nucleus of scientists experienced in the use of reactors for a wide range of scientific and technical problems. In addition to pursuing their own research and developing sophisticated experimental facilities, they actively seek out and encourage collaboration with other scientists engaged in challenging programs whose work can benefit from use of the reactor, but who as yet do not have the reactor experience necessary to take full advantage of the facilities available. The Division also provides irradiation services to a wide variety of users as well as engineering and other technical services.

The reactor operated at 10 MW during the past year and provided 25 experimental facilities ranging from intense neutron beams to extensive irradiation facilities, making it one of the most versatile high performance research reactors in the country. Thus, it is able to serve a large number of scientists and engineers in a broad range of activities both within and outside the NBS.

This report attempts to summarize all the work done which is dependent on the reactor including a large number of programs outside the Division. The first section summarizes these programs carried out by scientists in the Reactor Radiation Division and their collaborators. The second section summarizes NBS work originating entirely outside the Division which requires no collaboration with Division scientists. The section entitled, "Service Programs," covers those programs originating outside NBS but for which the Division provides irradiation services. The remaining sections are self-explanatory.

Appreciation is extended to F. J. Shorten of the Reactor Radiation Division for his extensive contributions to the editing, organization, and preparation of this report, and T. Lindstrom, P. Andrew, and S. Tassey for efforts in typing manuscripts.



R. S. Carter  
Chief, Reactor Radiation Division  
National Bureau of Standards

## ABSTRACT

This report summarizes all those programs which depend on the NBS reactor. It covers the period from July 1983 through June 1984. The programs range from the use of neutron beams to study the structure and dynamics of materials through nuclear physics and neutron standards to sample irradiations for activation analysis, isotope production, radiation effects studies, neutron radiography, and nondestructive evaluation.

Key words: Activation analysis; crystal structure; diffraction; isotopes; molecular dynamics; neutron; neutron radiography; nondestructive evaluation; nuclear reactor; radiation.

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## A. REACTOR RADIATION DIVISION AND COLLABORATIVE PROGRAMS

### THE INFLUENCE OF INDIVIDUAL REFLECTIONS IN LEAST SQUARES REFINEMENT

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The solution of a crystal structure is divided into two separate stages that may be called determination and refinement. Although least squares methods are used in both stages, it is only in the refinement stage that the statistical properties of least squares are significant. Drawing an analogy with a mathematically simple problem, determination corresponds to finding that a set of observations may be described by a linear function of some experimental variable, whereas refinement corresponds to precise determination of the values of the two parameters of that linear function. Determination that the function is linear requires observations for many values of the variable, but refinement is best achieved by careful measurements at the extremes of the accessible values of this variable.

To extend this principle to the multiparameter, non-linear models found in crystal structure analysis require some mathematical development. Designate by  $A$  the matrix with elements  $A_{ij} = [\partial M_i(\mathbf{x}) / \partial x_j] / \sigma_i$ , where  $M_i(\mathbf{x})$  is the model function for the  $i$ th observation and  $\sigma_i$  is its standard deviation. Let  $\mathbf{y}$  be the vector of observations. The least squares estimate of  $\mathbf{x}$  is  $\hat{\mathbf{x}} = (A^T A)^{-1} A \mathbf{y}$ , and the uncertainties of the elements of  $\hat{\mathbf{x}}$  are described by a variance-covariance matrix  $V = (A^T A)^{-1}$ . If  $V_n$  is the variance-covariance matrix after  $n$  observations, and  $\mathbf{z}$  is a row vector corresponding to the  $n + 1$ st row of  $A$ , the updated variance-covariance matrix after one more observation can be shown to be  $V_{n+1} = V_n - V_n \mathbf{z}^T \mathbf{z} V_n / (1 + \mathbf{z} V_n \mathbf{z}^T)$ . Thus, the diagonal elements of the matrix  $V_n \mathbf{z}^T \mathbf{z} V_n / (1 + \mathbf{z} V_n \mathbf{z}^T)$  are the amounts by which the  $n + 1$ st measurement will reduce the variance of the corresponding elements of  $\hat{\mathbf{x}}$ .

In the Single Crystal Intensity Project of the International Union of Crystallography, Hamilton and Abrahams<sup>1</sup> refined the structure of D(+) tartaric acid using ten different data sets collected by different laboratories, and found that the spread in values of refined parameters generally greatly exceeded what would be expected from the computed standard deviations. In their study, however, the standard deviations,  $\sigma_i$ , of the observations were not known, and were somewhat arbitrarily set to  $0.1 |F_o|$ . The belief was that this would produce weights that were approximately correct except for a scale factor that could be estimated from the overall goodness of fit, and that the reflections that departed from this would be

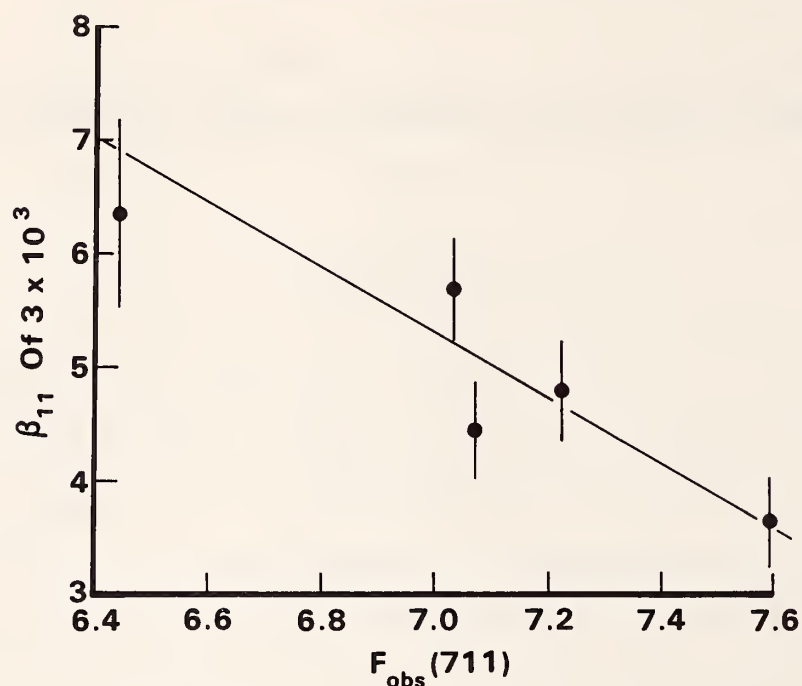


Figure 1. The value of  $B_{11}$  for atom O(3) in D(+) tartaric acid, plotted against the value of  $|F_o|$  of the 711 reflection for five different experiments. the determination of this parameter is dominated by this single reflection.

few in number and would not badly distort the refinement. A study of the influence of individual reflections on the various parameters has shown, however, that many parameters are determined by small sets of weak reflections whose standard deviations are underestimated in the weighting formula used. An extreme case is shown in Figure 1. here the value of  $B_{11}$  of atom O(3) is plotted against the value of  $|F_o|$  for the 711 reflection, corrected for extinction. The two are strongly correlated: this single reflection has a dominant influence on the determination of this parameter in these five experiments.

1. W. C. Hamilton and S. C. Abrahams, *Acta Cryst.* A26, 18 (1970).



# THE STRUCTURES OF THE TRANSITION ALUMINAS AND THEIR PRECURSORS

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The transition aluminas are a series of hydroxyl and microstructure stabilized materials which result from heating gibbsite, bayerite or boehmite. They are not true polymorphs of  $\text{Al}_2\text{O}_3$  but rather contain varying amounts of residual hydroxyl ions. The hydroxyl concentration, equivalent to a loss on ignition, ranges from more than 10% for "amorphous alumina" to less than 1% for the best crystallized high temperature phases like Theta and Kappa. The final high temperature product is the irreversible transformation to alpha alumina.

The low temperature products are often called activated aluminas in that they have high surface activity and very large specific surface areas. These materials are of high technological importance being widely used as catalytic substrates.

On heating the trihydroxides of aluminum, proton migration occurs, allowing the formation of water, which vaporizes. The resulting structure, and the role of the remaining hydrogens in stabilizing it, is unknown. It is reasonable to speculate that the layers  $\text{Al}(\text{OH})_6$  octahedra lose their interconnecting hydrogen bonds first, which induces the observed fine cracking in the material. In the first stage of heating the structurally ordered regions are on the order of 100 Å across, rendering the material x-ray amorphous. Diffusion and ion rearrangement follows, increasing the size of the structurally ordered regions. The reordering takes place within the framework of the original hydroxide crystal, and thus the starting material helps determine the structure at any subsequent temperature.

Structural information is desired on these materials because of their technological importance. However the minimal effect of hydrogen scattering on x-ray diffraction patterns has resulted in no information on the role of hydrogen in stabilizing these structures.

This investigation will look at each of the three aluminum hydroxides and the various transition products both in their hydrogen and deuterium forms using neutron diffraction. The pattern fitting Rietveld method will be used to structurally characterize these phases. Preliminary patterns of bayerite and eta alumina indicate that significant new information can be obtained from neutron powder diffraction. Analysis is continuing.

STRUCTURE STUDIES OF RHO ZEOLITES WITH UNUSUALLY SMALL UNIT CELLS

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and

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Dehydrated ND4-rho and Li-rho have been prepared with unit cell dimensions of 14.425(1) Å and 14.492(1) Å at 11 K (neutron refinement results). These are among the smallest cell constants determined for zeolite rho, substantially less than that previously determined for dehydrated H-rho at the same temperature (14.65 Å). Structural refinements are being carried out in order to determine the framework-cation interactions responsible for the small unit cell.

STUDIES OF ZEOLITES RHO AND ZK-5 PREPARED UNDER VARIOUS CONDITIONS

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Powder diffraction measurements were made on dehydrated samples of H-rho and ZK-5 prepared with calcination at 500°C and 650°C in such a way as to maximize the removal of framework aluminum atoms. Two phases were found in the data refinement for the sample of H-rho (500°C) with cell constants of 14.49 Å and 14.637(1) Å,  $1\bar{4}3m$ . H-rho (650°C) at 11 K shows an unusually large unit cell of 14.850(1) Å,  $Im\bar{3}m$ .

H-ZK5 (500°C) has a structurally well-characterized phase,  $a = 18.631(2)$  Å,  $Im\bar{3}m$ . H-ZK5 (650°C) is predominantly amorphous with the crystallographic phase having  $a = 18.440(7)$  Å,  $Im\bar{3}m$ .

The detailed structural reasons for the differences produced in the framework structure with calcination temperature are being studied.

STRUCTURAL AND MAGNETIC CHARACTERIZATION OF A NEW LAYERED  
ANTIFERROMAGNETIC COMPOUND,  $\text{LiFeMoO}_4\text{Cl}$ 

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Recently, the structure and magnetism of the new two-dimensional antiferromagnet  $\text{Fe(III)MoO}_4\text{Cl}$  was described.<sup>1</sup> In summary,  $\text{FeMoO}_4\text{Cl}$  has a layered structure consisting of sheets of corner-sharing  $\text{FeO}_4\text{Cl}$  square pyramids, site symmetry  $C_{4v}$ , bridged by  $\text{MoO}_4$  tetrahedra in tetragonal space group  $P4/nmm$ . Intralayer exchange leads to a broad 2D maximum in the magnetic susceptibility centered at 105 K while Mössbauer spectra confirm extended 3D antiferromagnetic ordering with a Néel temperature of 69.2 K.

The reaction of  $\text{Fe(III)MoO}_4\text{Cl}$  with  $\text{LiI}$  in acetonitrile (under inert atmosphere) yields  $\text{LiFe(II)MoO}_4\text{Cl}$ . This reversible reaction proceeds by a redox intercalation mechanism. Mössbauer spectra confirm the essential purity of this new phase and complete stoichiometric reduction of  $\text{Fe(III)MoO}_4\text{Cl}$ . x-ray powder diffraction data show that the new lithium intercalate is related to the starting tetragonal phase but possesses monoclinic symmetry. The Mössbauer parameters are consistent with five-coordinate, high-spin  $\text{Fe(II)}$  centers.  $\text{LiFeMoO}_4\text{Cl}$  has virtually the same 3D ordering temperature (68.5 K) as its precursor consistent with preliminary x-ray results that indicate a decrease in the interlayer spacing. The new lithium intercalate is also a 2D antiferromagnet but with somewhat weaker intralayer exchange than its precursor (i.e., the maximum in the magnetic susceptibility is centered at 73 K).<sup>2</sup>

In order to further characterize the structure of this novel layered antiferromagnetic intercalate (i.e., locate the lithium ions), room temperature neutron powder diffraction data have been collected and a structural refinement is currently in progress. If successful, a low temperature data set should give additional magnetic information.

- 
1. C. C. Torardi, J. C. Calabrese, K. Lázár, and W. M. Reiff, J. Solid State Chem. 51, 376 (1984).
  2. C. C. Torardi, K. Lázár, and W. M. Reiff, presented at the 1983 ACS National Meeting in Washington, D.C.



THE CRYSTAL STRUCTURES OF THE CHEVREL PHASES  $\text{Li}_{3.3}\text{Mo}_6\text{S}_8$  and  $\text{Li}_{3.2}\text{Mo}_6\text{Se}_8$

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The large class of ternary molybdenum chalcogenides of formula  $\text{M}_y\text{Mo}_6\text{X}_8$  (M = metallic element,  $0 \leq y \leq 4$ , X = S, Se, Te) has been of great interest due to unusual superconducting properties and extensive chemical variety of accommodation for the "ternary element" M. The basic structural building blocks are  $\text{Mo}_6\text{X}_8$  clusters consisting of eight X atoms forming the corners of a cube around the octahedron of six Mo atoms located near the cube face centers. The ternary elements are located between the  $\text{Mo}_6\text{X}_8$  clusters in positions which are on the line of the cluster cube diagonals (large M atoms), or displaced in sets of concentric rings centered about the cube diagonal (small ions). The small M ions may either be ordered or disordered in the rings.

We have employed neutron diffraction powder profile analysis to determine the crystal structures of the Chevrel phases  $\text{Li}_{3.3}\text{Mo}_6\text{S}_8$  and  $\text{Li}_{3.2}\text{Mo}_6\text{Se}_8$ . The  $\text{Mo}_6\text{X}_8$  cluster geometries are quite similar to those found in other compounds of this type, and the lithium atoms are randomly distributed over the inner and outer ring sites as found in other small ternary element phases. The lithium atoms show a strong preference in both compounds to occupy the outer ring sites. The  $\text{Cu}_x\text{Mo}_6\text{S}_8$  compounds also show a tendency to occupy the outer ring for large values of X, but to a much smaller degree. The geometry of the inner ring in  $\text{Li}_{3.2}\text{Mo}_6\text{Se}_8$  is similar to those found in other small ternary element phases but the inner ring in  $\text{Li}_{3.3}\text{Mo}_6\text{S}_8$  has a unique puckered configuration.

**POWDER NEUTRON DIFFRACTION STUDY OF ZIRCONIUM TITANATES**

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Zirconium titanate exists in a number of modifications. The pure compound,  $\text{ZrTiO}_4$ , gives a disordered  $\alpha\text{PbO}_2$ -like phase when quenched in water from temperatures above  $\sim 1150^\circ\text{C}$ , while a modulated structure is obtained by slow cooling from temperatures below  $1150^\circ\text{C}$ . With the addition of impurities, such as  $\sim 1\%$  of  $\text{Y}_2\text{O}_3$ , the compound  $\text{Zr}_{0.95}\text{Ti}_{0.05}\text{O}_{2.4}$  is formed. This phase is orthorhombic with the a-axis about three times that of the pure compound quenched in water. We have analyzed so far two phases of zirconium titanate with the neutron powder technique and the Rietveld method. Some of the results are briefly described in what follows.

#### $\text{ZrTiO}_4$ Quenched in Water

Lattice parameters measurements indicate that this form may be isomorphous with ixiolite (space group Pbcn, general formula  $\text{MO}_2$ , and  $Z = 4$ ). In this model Zr and Ti must be completely disordered in the 4c2 positions, i.e.,

$$M = (1/2) \text{Zr} + (1/2) \text{Ti}$$

A refinement with the initial parameters of ixiolite gave  $R_N = 14.07$ ,  $R_P = 7.54$ ,  $R_W = 9.61$ , and  $R_E = 5.01$ . Although these results indicate that the structure is basically disordered, the rather high value of  $R_N$  may reflect a slight ordering of the metal atoms. Refinements were therefore attempted using models in which partial or total ordering of the Zr and Ti atoms is possible.

In the first of such refinements the structure was assumed to be isomorphous with wolframite (space group  $P2_1/c$ , general formula  $\text{ABO}_4$ , and  $Z = 2$ ). For this case

$$A = x\text{Zr} + (0.5-x)\text{Ti}$$

$$B = (0.5-x)\text{Zr} + x\text{Ti} \quad 0 \leq x \leq 0.5$$



with A and B in positions 2e2. Results show that the best agreement is obtained with  $x = 0.5$ , i.e., with a completely disordered structure, and no improvement with respect to the first refinement was obtained.

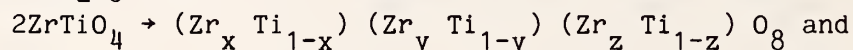
Refinements were also carried out using a model isomorphous with tantalite (space group Pbcn, general formula  $AB_2O_6$ , and  $Z = 4$ ). It is easy to show that, in this case

$$A = xZr + (1-x) Ti$$

$$B = (0.75 - \frac{x}{2}) Zr + (0.25 + \frac{x}{2}) Ti \quad 0 \leq x \leq 1.0$$

and with A in positions 4c2 and B in positions 8d1. Here again, the best agreement was obtained for the disordered structure ( $x = 0.5$ ).

One last possibility is a model isostructural with wodginite (space group C2/c, general formula  $ACB_2O_8$ , and  $Z = 4$ ). We may write for this case



$$A = xZr + (1-x) Ti$$

$$C = yZr + (1-y) Ti$$

$$B = [1-(x+y)/2]Zr + [(x+y)/2]Ti$$

where

$$0 \leq x \leq 1.0, \quad 0 \leq y \leq 1.0, \quad \text{and} \quad 0 \leq (x+y) \leq 2.0.$$

These refinements are not yet complete, but the indication is that the structure does not have any wodginite-type of ordering.

#### $Zr_5Ti_7O_{24}$ With Slow Cooling

Lattice parameters and peak intensities indicate that this compound is isostructural with tantalite. Remembering the general formula  $AB_2O_6$  we have

$$A = xZr + (1-x) Ti$$

$$B = (0.625 - x/2) Zr + (0.375 + \frac{x}{2}) Ti \quad 0 \leq x \leq 1.0$$

The best agreement between calculated and observed intensities was obtained for  $x = 1.0$ , with  $R_N = 10.05$ ,  $R_P = 7.40$ ,  $R_W = 9.35$ , and  $R_E = 4.49$ . The structure is completely ordered. The crystallochemical features of this structure are still being analyzed.

NEUTRON DIFFRACTION STUDY OF ZIRCONIUM PALLADIUM DEUTERIDE,  $\text{Zr}_2\text{PdD}_{<2}$ 

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$\text{Zr}_2\text{Pd}$  which has the tetragonal  $\text{MoSi}_2$  structure, reacts readily with hydrogen at room temperature to form hydrides (Maeland, J. Less-Common Met. (1983), 89, 173-182). There are several potential interstitial sites for hydrogen in the  $\text{MoSi}_2$  structure. We have used neutron diffraction to establish which sites are occupied. Three compositions were studied  $\text{Zr}_2\text{PdD}$ ,  $\text{Zr}_2\text{PdD}_{1.71}$ , and  $\text{Zr}_2\text{PdD}_{1.98}$ . The structures were refined by the method of total profile analysis of the neutron diffraction powder patterns. The D atoms are located at the center of distorted tetrahedra of Zr atoms in all these samples. The results for  $\text{Zr}_2\text{PdD}_{1.71}$  are representative. Space group  $I4/mmm$ ,  $Z = 2$ ,  $a = 3.3208(2)\text{\AA}$ ,  $c = 11.606(1)\text{\AA}$ . The atomic coordinates are: Pd at 000 (2(a) positions), Zr at 00z (4(e) positions) with  $z = 0.3565(2)$  and D at  $0\ 1/2\ 1/4$  (4(d) positions). Temperature factors were 0.4 for Pd and Zr and 1.0 for D. Final R factors:  $R_N = 9.53$ ,  $R_p = 7.11$ ,  $R_w = 9.06$ , and  $R_E = 5.80$ .

A NEUTRON DIFFRACTION AND A/C CONDUCTIVITY STUDY OF  $\text{Pb}_{1.5}\text{Ta}_2\text{O}_{6.5}$ 

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There has been considerable interest in recent years in defective pyrochlore structured compounds. This class of compounds of general formula  $\text{A}_2\text{B}_2\text{O}_7$ , has an anion deficient fluorite structure with an ordered cation arrangement. Much of the interest in these materials is due to their high oxygen ion conductivities. The present study concerns a particularly intriguing defect pyrochlore,  $\text{Pb}_{1.5}\text{Ta}_2\text{O}_{6.5}$ . This compound has been the subject of previous investigations which have left unresolved the questions relating to the composition width, and the defect structure of the material. These problems were examined in the present study carried out by powder neutron diffraction and by electrical conductivity measurements.

The neutron intensity data were analysed using the Rietveld profile refinement techniques. All peak shapes (including those at low angle) are accurately Gaussian, making use of the Rietveld technique appropriate. The refinement assumed a defective pyrochlore structure (space group  $Fd\bar{3}m$ ) with Pb vacancies on the 16d sites and oxygen vacancies on the 8(a) sites. Occupation numbers of Pb and oxygen 8(a) sites were refined as were the temperature factors. Unlike an earlier x-ray study, separate temperature factors were used for the two types of oxygen sites.

The following results of the refinements deserve note:

(i) The refined occupation numbers are very close to those expected for 50 percent vacancies on the oxygen 8(a) sites and 28 percent vacancy on the Pb sites.

(ii) The temperature factors for Pb and more specially the oxygen 8(a) sites are high suggesting a considerable static displacement around these sites.

(iii) In contrast, the temperature factors for the Ta and oxygen (48f) sites are normal suggesting that these sites are not strongly perturbed by the introduction of vacancies.

We should also note that refinements were attempted with different Pb and oxygen 8(a) occupation numbers and with these atoms displaced from these sites. In every case, a higher R-factor was obtained thus underpinning the stoichiometry of the phase and also illustrating that while static displacements of the lead and oxygen ions are observed no coherent long range displacements exist.

A key factor in causing the small composition width of this highly defective phase may be the stabilization of anion vacancies by the lone pairs on the neighboring  $Pb^{2+}$  ions.

THE STRUCTURES OF LITHIUM INSERTED METAL OXIDES:  $\text{Li}_{.5}\text{TiO}_2$  (ANATASE),  $\text{LiTi}_2\text{O}_4$  (SPINEL), AND  $\text{Li}_2\text{Ti}_2\text{O}_4$

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Transition metal oxides with tunnel or framework structures have been investigated extensively as hosts for lithium insertion at room temperature. Compounds based on  $\text{TiO}_2$  provide a variety of such structures having related chemistry and different host geometries. Both the Brookite and Rutile forms of  $\text{TiO}_2$  react with only small amounts of Li. In contrast, the Anatase and  $\text{TiO}_2(\text{B})$  forms have been found to react extensively, to about .7 Li/Ti, on reaction with n-BuLi, or on electrochemical insertion of Li. The host structure of Anatase is originally tetragonal and becomes orthorhombic on Li insertion. The product,  $\text{Li}_{.5}\text{TiO}_2$ , is obtained on reaction of n-BuLi with Anatase under mild conditions, and on heating to 450-500°C transforms from the orthorhombic phase to a cubic phase with a crystallographic unit cell and electrical properties identical to those of the  $\text{LiTi}_2\text{O}_4$  phase synthesized at high temperatures. Reaction of this cubic phase  $\text{LiTi}_2\text{O}_4$  with n-BuLi results in the accommodation of additional lithium, to a stoichiometry of  $\text{Li}_2\text{Ti}_2\text{O}_4$ , with only a small change in the cubic unit cell dimension.

In this report we elucidate the results of our structural studies of the compounds  $\text{Li}_{.5}\text{TiO}_2$  (anatase), of the  $\text{LiTi}_2\text{O}_4$  cubic phase prepared by heating  $\text{Li}_{.5}\text{TiO}_2$  above 450°C, and of the  $\text{Li}_2\text{Ti}_2\text{O}_4$  product obtained by lithiation of the cubic  $\text{LiTi}_2\text{O}_4$  phase at ambient temperature. The structures of all three phases were determined by neutron diffraction powder profile analysis, as single-crystal of these materials are not available.

We have found that the inserted Li ions occupy partially the octahedral interstices in the highly distorted CCP oxygen array of Anatase  $\text{TiO}_2$ . Within those interstices, their coordination is closer to 5 than to 6 fold, and their addition to the structure decreases somewhat the distortion of the host. The limiting stoichiometry of .7 Li/Ti is, therefore, not due to the number of available interstitial sites (there is 1/Ti) but rather must be related to the strong mutual interactions of the ions occupying those sites. Further, we have found that the



distortion from tetragonal to orthorhombic is due to the formation of zig-zag chains of Ti-Ti bonds, and that the non-metallic resistivity of the Li-anatase can be attributed to localized electrons. On heating above 450°C, the compound becomes electrically conductive, the structure changes to a spinel type  $\text{LiTi}_2\text{O}_4$  with the coordination of Li changing from 5 to 4 fold. In this phase of the bonding is very regular and the anion array is distorted only slightly from ideal CCP. The  $\text{LiTi}_2\text{O}_4$  phase formed at elevated temperatures has been assumed in the past to have the spinel structure without direct confirmation until this time.

On further lithiation of the  $\text{LiTi}_2\text{O}_4$  phase at ambient temperature, the lithium is displaced and vacates completely the tetrahedrally coordinated interstices and fills the octahedrally coordinated interstices of the  $\text{TiO}_2$  host to a stoichiometry of  $\text{Li}_2\text{Ti}_2\text{O}_4$ . This radical change in Li site occupancy explains the large drop in EMF observed in the electrochemical insertion of Li into  $\text{LiTi}_2\text{O}_4$ . The structure of  $\text{Li}_2\text{Ti}_2\text{O}_4$  may be thought of as an ordered rocksalt type, with the CCP oxygen array insignificantly distorted from ideal and the cation-oxygen bonding quite regular.

#### STRUCTURE OF BOVINE PANCREATIC TRYPSIN INHIBITOR

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The structure of deuterated crystals of form II of BPTI (space group  $P2_12_12_1$ ,  $a=74.1\text{\AA}$ ,  $b=23.4\text{\AA}$ ,  $c=28.9\text{\AA}$ ) has been refined using x-ray diffraction data extending to  $1.0\text{\AA}$ , as well as  $1.8\text{\AA}$  neutron diffraction data. x-ray intensities were collected in Munich using standard diffractometry (Walter and Huber, 1983). The number of observed x-ray intensities used in the refinement was 17,615. Neutron diffraction data were collected from a large crystal (volume  $\sim 8\text{mm}^3$ ) which was deuterated by slow exchange of its mother liquor for 3 months. The flat-cone diffractometer at NBS was used for the neutron data collection and each reflection was measured at least three times, with a complete data set requiring about four months of instrument time. The

reflection intensities were integrated using a dynamic mask procedure (Sjölin and Wlodawer, 1981). Symmetry R factors ranged from 0.048 for lower levels to 0.126 for the level  $k=10$ , while the scaling R factor for the flat-cone and equatorial data was 0.076. The total number of unique observed reflections was 4044 (78% of the theoretical maximum), with over half of the reflections observed in the shell at 1.82Å resolution.

Joined restrained refinement using both types of data utilized the procedures of Wlodawer and Hendrickson (1982). Computer graphics were used between refinement cycles to make larger corrections to the model. The R factors for the final model were 0.200 (x-ray) and 0.197 (neutron). The bond lengths differed from the ideal values by 0.02Å, the departure from planarity was 0.019Å, and the chiral volumes differed by 0.232Å<sup>3</sup>. We were able to place almost all hydrogens, including the methyl rotors, which were uniformly found in staggered conformations. We found that 11 out of 54 amide hydrogens were protected from exchange during the course of the experiment. Nine of the protected hydrogens were involved in forming  $\beta$ -sheet hydrogen bonds, one made a hydrogen bond to a side chain, while protection of Gly37 was caused by its interaction with the ring of Tyr35 (Figure 1). This type of

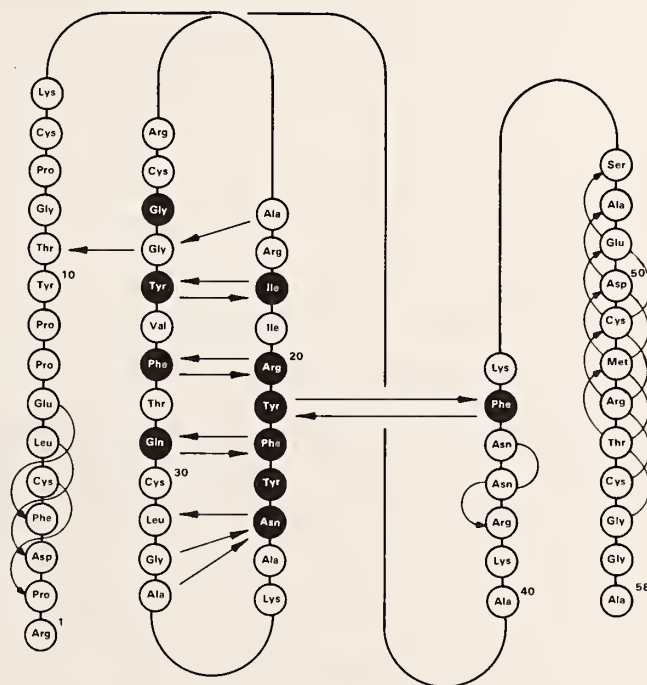


Figure 1. Diagram of hydrogen bonds involving the main-chain atoms and the level of protection of amide hydrogens. Only bonds shorter than 3.15 Å and with expected angles are shown. Filled circles correspond to protected amide hydrogens.

protection has not been previously reported in the literature. The agreement between the extent of hydrogen exchange observed in this study and the 2-D NMR results of Wagner and Wüthrich (1982) is excellent, offering the first independent confirmation of the latter technique.

The presence of neutron diffraction data allowed us to reconsider the orientation of the side chain of Glu31, to place the deuteriums in hydroxyls of side chains such as theonines, tyrosines and serines, and contributed to the correct placement of the two residues at the carboxyl terminus of the protein, which were not visible in the initial x-ray maps.

The comparison of the new model with that for crystal form I shows r.m.s. deviation between equivalent main chain atoms at 0.4Å. Deviations exceeding 0.5Å were observed near both termini, at the alpha carbons of Lys15, Lys26, Leu29, and in stretches of residues 16-19, 39-41, and 47-50. These deviations are most probably due to crystal packing forces and their analysis should lead to better understanding of the reasons for reported discrepancies between the crystallographically refined structures of proteins and between the structures which were energy minimized.

The analysis of solvent structure yielded 63 ordered water molecules and one phosphate group. Half of the solvents have full occupancy, while the least occupied solvent sites which could be assigned above the noise level contained about 0.4 water molecules. It is clear that the analysis of solvent is in need of further improvement.

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THE PRESSURE DEPENDENCE OF THE BARRIER TO METHYL GROUP REORIENTATION  
IN SOLID NITROMETHANE

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Nitromethane in the solid state has proven to be a prototypical system for the study of the properties of the barrier to rotation of a molecular group. In one sense it is the simplest system available for such studies since it consists of a single one-dimensional rotor with the same crystallographic phase for both the protonated and deuterated species from the melt to 4.2°K, thus making the interpretation of spectroscopic results relatively straightforward. On the other hand, it has proven quite interesting and less than simple in that a simple potential has not been found which explains entirely the measured level scheme, and the measured activation energy for thermally activated notation of the methyl group.

In previous work<sup>1</sup> the crystal structure and several dynamical properties of both the protonated and deuterated species have been measured. In particular, the crystal structure investigation has determined there is one formula unit in the asymmetric unit leading to but one potential of three-fold symmetry hindering reorientation. Since the barrier to re-orientation due to intramolecular interactions is extremely small<sup>2</sup>, the barrier observed in the solid will be dominated by intermolecular interactions. The dynamical properties which had been determined for the protonated isotopic species included the activation energy for thermally activated reorientation, and for both isotopic species the quantum mechanical tunnel splitting of the ground state and the position of the first excited state. The present work was motivated as an attempt, by the application of pressure, to change the position of the first excited states with respect to the top of the barrier thereby changing their width in order to confirm the assignment.

The measurements of the pressure dependence of the first excited state of  $\text{CH}_3\text{NO}_2$  were performed with the triple axis spectrometer located at BT4 of the NBS research reactor. The instrument was configured to produce 1 meV resolution at an energy transfer of 7 meV. The pressure transmitting medium was He gas. The sample container<sup>3</sup> was cylindrical of dimension 2.4 mm interior diameter and 7.9 mm outside diameter and was connected to the intensifier by a small capillary. A manganin gauge



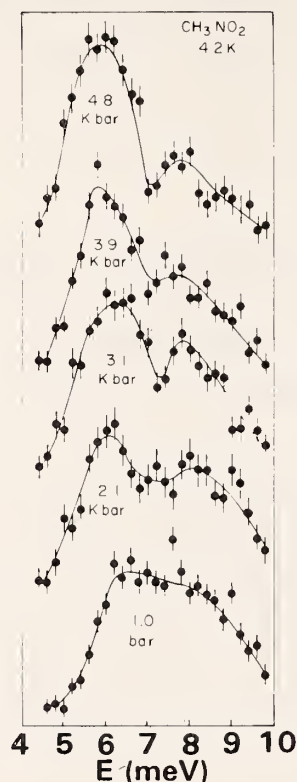


Figure 1. Inelastic neutron scattering spectrum of  $\text{CH}_3\text{NO}_2$  at 4.2 K and various pressures

was used to measure the pressure which was applied before the sample was cooled to 4.2°K. A survey run ( $4.4 \leq \Delta E \leq 14$  meV) with the sample pressurized to 4.8 Kbar showed that no prominent features in the spectrum existed above 10 meV. Subsequent data was obtained only in the energy region from 4.4 to 10 meV. The results of the various measurements are presented in Figure 1. Our interpretation of the features exhibited there is as follows. The peak at lower energy which moves from ~ 6.6 meV at ambient pressure to 5.8 meV at 4.8 Kbar is due to the unresolved first excited states. The higher energy feature at 7.8 meV which does not shift with pressure is assigned to a density of phonon states. We are led to this assignment due to: (a) a correct assignment by a Raman study<sup>4</sup> of the torsion mode to 6.6 meV at ambient pressure (as opposed to our previous assignment to 6.6 and 8.4 meV); (b) the fact that this peak is the most pressure dependent; and (c) a feature at ~ 7.8 meV in the spectrum of  $\text{CD}_3\text{NO}_2$  which is clearly due to phonon density of states<sup>1</sup>. We are left, however, with a negative Gruneisen constant implying a lowering of the barrier with pressure.

An additional measurement which yields information concerning the barrier is the tunnel splitting of the ground state. These measurements were performed at the

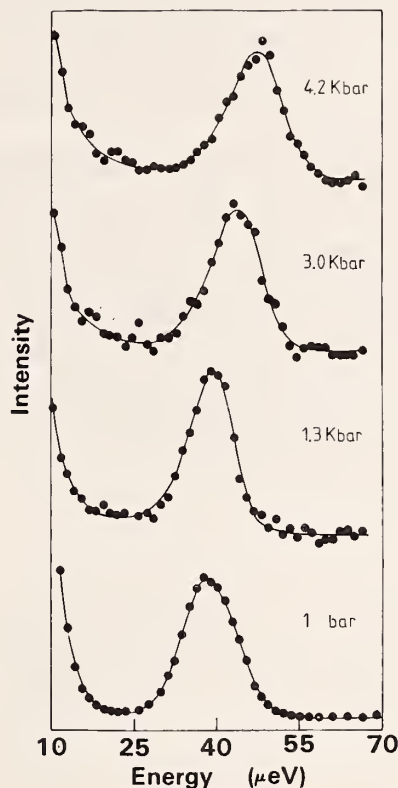


Figure 2. Inelastic neutron scattering spectrum of  $\text{CH}_3\text{NO}_2$  at 4.2K and various pressures.

research reactor at the ILL. Figure 2 presents the results of these measurements as a function of pressure. Note that the tunnel splitting increases with increasing pressure, an effect opposite to that observed in all previous studies of the pressure dependence of tunnel splitting in other systems<sup>5</sup>.

A search for a potential of the form

$$V(\phi) = \frac{V_3}{2} (1 - \cos 3\phi) + \frac{V_6}{2} (1 - \cos 6\phi)$$

which would explain this data resulted in the following values for  $V_3$  and  $V_6$ . At 1 bar,  $V_3 = 26$  meV,  $V_6 = 10.25$  meV which produced a ground state splitting of 33 peV and a first excited state at 7.2 meV in very good agreement with observations. At 4.8Kbar,  $V_3 = 26$  meV and  $V_6 = 14.5$  meV resulting in a ground state splitting of 45 peV and a first excited state at 5.8 meV. This potential correctly reproduces the behavior of the energy levels with pressure. It also, however, predicts a second bound level at ~16.5 meV. A search for such a level was conducted using the time-of-flight instrument at ILL at a temperature of 4.2K°. In addition to the peaks at 2 meV due to the first excited state, there was found one at ~18 meV which is assigned to the bound search excited state predicted by the model.

## REACTOR RADIATION DIVISION AND COLLABORATIVE PROGRAMS

We have now to explain an activation energy to thermally activated rotation of ~10 meV, substantially less than the barrier height of ~24 meV predicted by the single particle potential which so successfully explains the measured level scheme and its pressure dependence. This phenomena, using an activation energy lower than a bound state is not unknown. It is a common occurrence in hydrogen in metals. The mechanism of "phonon assisted tunneling" is invoked, in which a cooperative motion of the metal atom when a phonon is thermally activated results in relaxing the cage surrounding the hydrogen such as to enhance diffusion. A similar mechanism must be at work in this system and to our knowledge it is the first instance of rotating molecular groups exhibiting such behavior.

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## CRYSTALLOGRAPHIC AND MICROSTRUCTURAL CHARACTERIZATION OF URANIUM ALLOYS

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Alloys of uranium can be produced which possess a variety of mechanical properties ranging from very soft, low strength materials to extremely hard, high strength materials. The crystallographic and microstructural properties of depleted uranium alloys (0.75 wt. % Ti) with two different heat-treatments, "depleted uranium as cast" (DUAC) and "depleted uranium with heat treatment" (DUHT), were studied by neutron powder diffraction methods. The pole figures of both DUAC and DUHT samples

Table 1. Structural Parameters of DUHT and DUAC Compared with Those of Pure Uranium

(a) Cell dimensions (space group Cmc<sub>2</sub>m)

| <u>Sample</u>     | <u>DUHT</u> | <u>DUAC</u> | <u>Pure-U (<math>\alpha</math>-U) (Cooper, 1962)</u> |
|-------------------|-------------|-------------|------------------------------------------------------|
| $a(\text{\AA})$   | 2.8610(1)   | 2.8574(1)   | 2.85373(5)                                           |
| $b(\text{\AA})$   | 5.8234(2)   | 5.8537(2)   | 5.87010(6)                                           |
| $c(\text{\AA})$   | 4.9736(2)   | 4.9640(2)   | 4.95573(6)                                           |
| $V(\text{\AA}^3)$ | 82.86(1)    | 83.03(1)    | 83.017(1)                                            |

(b) Positional Parameters

| <u>Sample</u> | <u>DUHT</u> | <u>DUAC</u> | <u>Pure-U (<math>\alpha</math>-U) (Lander, et al 1970)</u> |
|---------------|-------------|-------------|------------------------------------------------------------|
| x             | 0.          | 0.          | 0.                                                         |
| y             | 0.1028(1)   | 0.1025(1)   | 0.1027(3)                                                  |
| z             | 0.25        | 0.25        | 0.25                                                       |

(c) Bond lengths and angles of the corrugated layer

| <u>Sample</u>   | <u>DUHT</u> | <u>DUAC</u> | <u>Pure-U*</u> |
|-----------------|-------------|-------------|----------------|
| zig-zag bonding | 2.760(1)    | 2.757(1)    | 2.756          |
| a-axis bonding  | 2.8610(1)   | 2.8574(1)   | 2.8537(1)      |
| zig-zag angle   | 128.6(1)    | 128.4(1)    | 128.1          |

\*based on Cooper's cell and Lander et al.'s positional parameters.



(d) Inter-layer atomic distances

| <u>Sample</u>      | <u>DUHT</u> | <u>DUAC</u> | <u>Pure-U</u> |
|--------------------|-------------|-------------|---------------|
| primary distance   | 3.2441(2)   | 3.2569(2)   | 3.2635        |
| secondary distance | 3.342(1)    | 3.344(1)    | 3.342         |

(e) The coefficients of the width function  $H^2 = U \cdot \tan^2 \theta + V \cdot \tan \theta + W$ , where  
H is in  $0.01^\circ$  unit.

| <u>Sample</u> | <u>DUHT</u> | <u>DUAC</u> |
|---------------|-------------|-------------|
| U             | 7619(295)   | 4372(163)   |
| V             | -4274(271)  | -3582(116)  |
| W             | 1980(80)    | 1736(43)    |

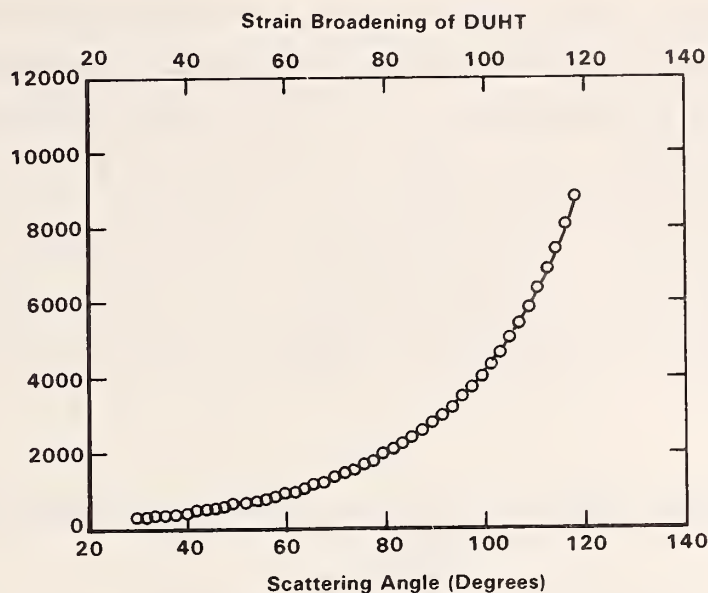


Figure 1. The strain broadening of DUHT as a function of scattering angle. The observed broadening [ $H^2(\text{DUHT}) - H^2(\text{DUAC})$ ] are indicated by the circles, and the predicted broadening curve after the least-squares fit by the solid line.

showed no evidence of systematic texture. The neutron diffraction patterns of the polycrystalline samples were measured with the high-resolution powder diffractometer using 10', 20', 10' collimations. To eliminate local texture or coarse grain effects, the samples were spun constantly at 1 r.p.m. during the measurements. The crystal structures, lattice parameters, and the coefficients of the width function were refined by Rietveld's profile refinement method. The residuals,  $R_{wp}$ ,  $R_e$ , and  $R_B$  were 9.2%, 7.2%, and 3.9% for DUHT and 8.4%, 6.9%, and 3.0% for DUAC. The results are summarized in Table 1.

The crystallographic structures of DUAC and DUHT are essentially the same as that of pure uranium. However, the unit cell dimensions are quite different. The deformation of the DUHT cell (from the pure uranium) is much larger in magnitude but very similar in deformation mode to DUAC, which is attributed to the super-saturated Ti impurities in the lattice. A comparison of the unit cell volumes suggests that the Ti impurity in DUHT is mostly of the substitutional type.

#### Residual Stress Analysis by Width Function

The width function,  $H(\theta) = U \tan^2 \theta + V \tan \theta + W$ , obtained from the DUHT sample was much broader than, but that of DUAC was in reasonable agreement with, those of standard samples (e.g.,  $\text{Al}_2\text{O}_3$  or Cu powder). Therefore, it is assumed that the width function of the DUHT is a convolution product of three Gaussian functions:

instrumental resolution, strain distribution, and particle size distribution. Using the width function of the DUAC for the instrumental resolution, the r.m.s. strain  $\langle e \rangle^{1/2}$  and the particle size dimension  $L$  for the DUHT were determined by a non-linear least squares refinement of the broadening function,  $\Delta H$ :

$$\Delta H^2 = (\pi/2) \cdot \langle e \rangle^{1/2} (4 \tan \theta)^2 + [\lambda / (L \cos \theta)]^2$$

$$\text{where } \Delta H^2 = H^2 (\text{DUHT}) - H^2 (\text{DUAC}).$$

The results were  $\langle e \rangle^{1/2} = 0.00188(1)$  and  $L = 1.2 (9) \times 10^5 \text{ \AA}$ . The observed and calculated width functions are shown in Figure 1.

### CRYSTALLOGRAPHIC STUDY OF POLYNITRO-BISHOMOCUBANE

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and

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There is considerable current interest in the synthesis and chemistry of strained energetic compounds. Polynitropolycyclic compounds are potential members of this important class. However, very few nitro-containing polycyclic "cage" compounds have been synthesized. This report consists of two independent studies for the newly synthesized compounds: the crystal structure determination of trinitro-bishomocubane, and the crystal structure determination of tetranitro-bishomocubane.

#### 1. The crystal structure of trinitro-bishomocubane

H. L. Ammon, C. S. Choi, O. Sandus, A. P. Marchand, and S. C. Suri

The space group determination was made on the basis of precession photographs, from which a monoclinic  $P2_1$  structure with  $a = 9.349(4)$ ,  $b = 7.400(3)$ ,  $c = 16.007(10) \text{ \AA}$ ,  $\beta = 97.78(4)^\circ$ , and four molecules per cell were obtained. The crystal density, based on the x-ray unit cell, is  $1.61 \text{ g/cm}^3$ . The crystal structure was determined from 1339 reflection intensities measured by single crystal x-ray diffraction. The molecular structure is shown in Figure 1. The carbon cage of the molecule consists of four puckered 5-membered rings and two 4-membered rings. The average bond lengths and bond angles are summarized in Tables 1 and 2. The structure will be discussed later, comparing with that of tetranitro-bishomocubane.

#### 2. The crystal structure of tetranitro-bishomocubane

C. George, R. Gilardi, J. Flippen-Anderson, C. S. Choi, A. P. Marchand, and  
D. S. Reddy

The preliminary study of the crystal symmetry by precession photographs indicated that the space group is monoclinic,  $Pc$  or  $P2/c$ , with  $a = 7.761(1)$ ,  $b = 11.500(2)$ ,  $c = 14.277(2)$ ,  $\beta = 108.63(2)$ , and four molecules per unit cell. The density calculated from the unit cell data is  $1.72 \text{ g/cm}^3$ . The non-centrosymmetric space group  $Pc$  was proven to be correct by the final crystal structure determination. There are two crystallographically distinct molecules in the crystal, which we designate as molecules A and B. The ORTEP drawings of the molecules are given in Figure 2. The average bond lengths and angles are summarized in Tables 1 and 2.

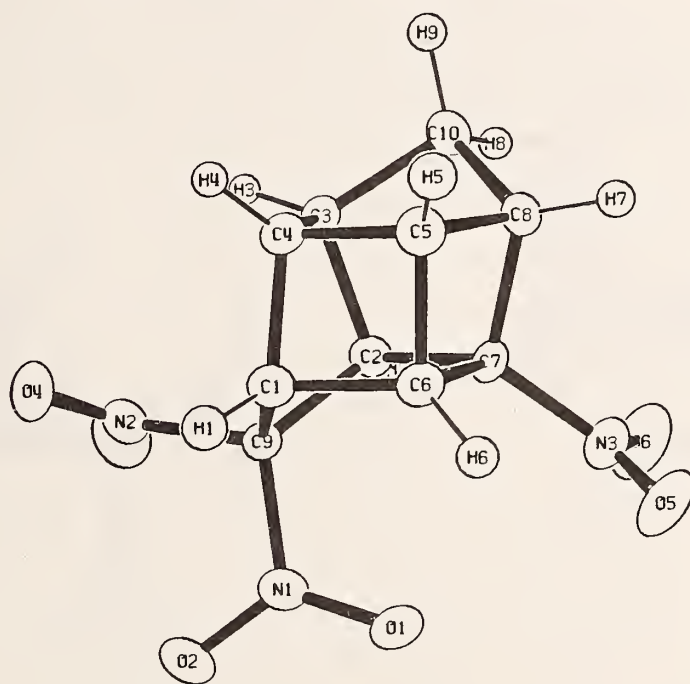


Figure 1. ORTEP drawings of trinitro-bishomocubane molecule.

Table 1. The average bond lengths and the maximum spread from the mean.

| Compounds       | $C_{10}H_9(NO_2)_3$ | $C_{10}H_8(NO_2)_4$ |                 |
|-----------------|---------------------|---------------------|-----------------|
|                 |                     | (A)                 | (B)             |
| C-C bonds       |                     |                     |                 |
| Bridging C-atom | 1.52 $\pm$ 0.01     | 1.52 $\pm$ 0.02     | 1.52 $\pm$ 0.02 |
| Cubane skeleton | 1.55 $\pm$ 0.03     | 1.55 $\pm$ 0.02     | 1.55 $\pm$ 0.03 |
| C-N bonds       |                     |                     |                 |
| C7-N            | 1.48                | -                   | -               |
| C9-N            | 1.51/1.52           | 1.51/1.52           | 1.52/1.51       |
| C10-N           | -                   | 1.51/1.53           | 1.52/1.52       |
| N-O bonds       | 1.21 $\pm$ 0.02     | 1.20 $\pm$ 0.01     | 1.19 $\pm$ 0.01 |



Table 2. The average bond angles and the maximum spread from the mean.

| Compounds          | $C_{10}H_9(NO_2)_3$ | $C_{10}H_8(NO_2)_4$ |                 |
|--------------------|---------------------|---------------------|-----------------|
|                    |                     | (A)                 | (B)             |
| C-C-C ( $^\circ$ ) |                     |                     |                 |
| 4-membered ring    | $89.1 \pm 0.26$     | $89.2 \pm 2.8$      | $89.2 \pm 3.2$  |
| 5-membered ring    | $103.7 \pm 5.7$     | $103.4 \pm 3.7$     | $103.4 \pm 3.5$ |
| Bridging C-atom    | $96.9 \pm 1.3$      | $97.9 \pm 0.2$      | $98.3 \pm 0.2$  |
| O-N-O ( $^\circ$ ) | $124.8 \pm 1.3$     | $125.3 \pm 0.8$     | $125.2 \pm 1.6$ |

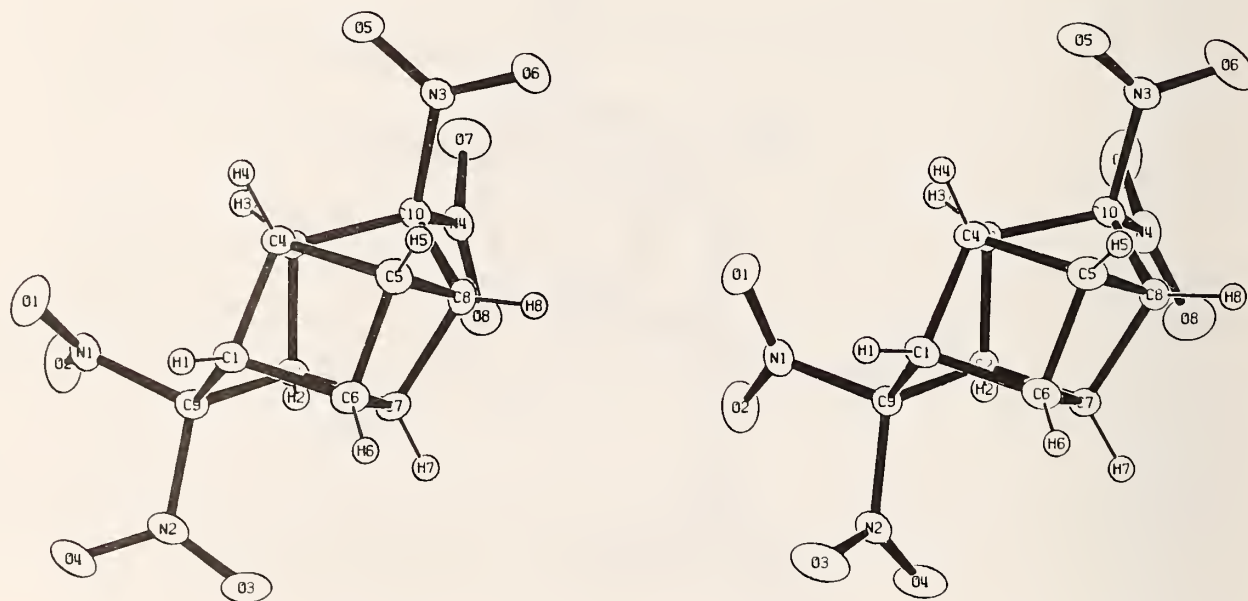


Figure 2. ORTEP drawings of tetranitro-bishomocubane molecules.

The carbon skeleton (bishomocubane) of the three molecules in the tables consists of four puckerd 5-membered rings and two 4-membered rings. The 4-membered rings are all bent about their diagonals by approximately  $20^\circ$  which causes the average c-c-c angles to be  $89.1^\circ$  or  $89.2^\circ$ , instead of  $90^\circ$ . The bond angles of the bridging carbon are distinctly smaller than others within each 5-membered ring. Similarly, the bond lengths of the bridging carbons are consistently shorter than others within the same ring by about  $0.03 \text{ \AA}$  for all three molecules. The C-N bond length of the C(7) carbon with one  $NO_2$  group attachment is  $1.48 \text{ \AA}$ , but those of other carbons with two  $NO_2$  groups each are considerably longer, approximately  $1.52 \text{ \AA}$  on the average. This suggests that the number of electron withdrawing groups on the same carbon atom is related to the elongation of the C-N bond. There are no unusual intermolecular contacts and no evidence of hydrogen bonding.

## SIMULATION OF THE INITIATION OF DETONATION IN AN ENERGETIC MOLECULAR CRYSTAL

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Detonation in a chemically reactive system has been extensively studied from the viewpoint of continuum mechanics under the assumption of local equilibrium in all thermodynamic parameters except chemical composition.<sup>1,2</sup> In a steady detonation wave, this means that the various energy relaxation processes are assumed to occur at a rate at least equal to the local sound velocity. Pastine et al.,<sup>3</sup> however, have pointed out that the average frequency of the intramolecular vibrations in a dense system may be expected to be much higher than that of the intermolecular vibrations, and consequently the relaxation processes for energy transfer between V-R, V-T, and R-T (V = vibrational, R = rotational, T = translational) degrees of freedom should be rather slow. Assuming a constant relaxation time  $\tau_R$ , Pastine et al. constructed a simple model of shock initiation of detonation which predicted an initiation time controlled by  $\tau_R$ , and hence by the duration of the shock pulse, in good agreement with experiment for one material. But for a different material they obtained poor agreement.

The problems of energy relaxation are of very general interest in physics and chemistry. With the development of lasers, computers and chemical studies in the picosecond regime, studies of these problems have become more interesting because it is now possible to investigate the energy transfer processes on the time scale of real chemical reactions. The initiation of detonation is of special interest because it is a limiting case of an extremely fast reaction, its time scale ( $10^{-13}$  to  $10^{-10}$  s) matching well the time scale of molecular dynamical (MD) computations. For these reasons, and as a contribution toward answering some of the questions raised by Pastine et al., we have carried out an MD study of the initiation and propagation of detonation in a model of an energetic molecular crystal. Our results show for the first time the initiation and propagation of the reaction on a molecular scale. They also show the energy transfer processes to be much slower than sound propagation, in qualitative agreement with Pastine et al. These results contain many details of the molecular motion and of the mechanisms of thermal and shock initiation. Moreover,

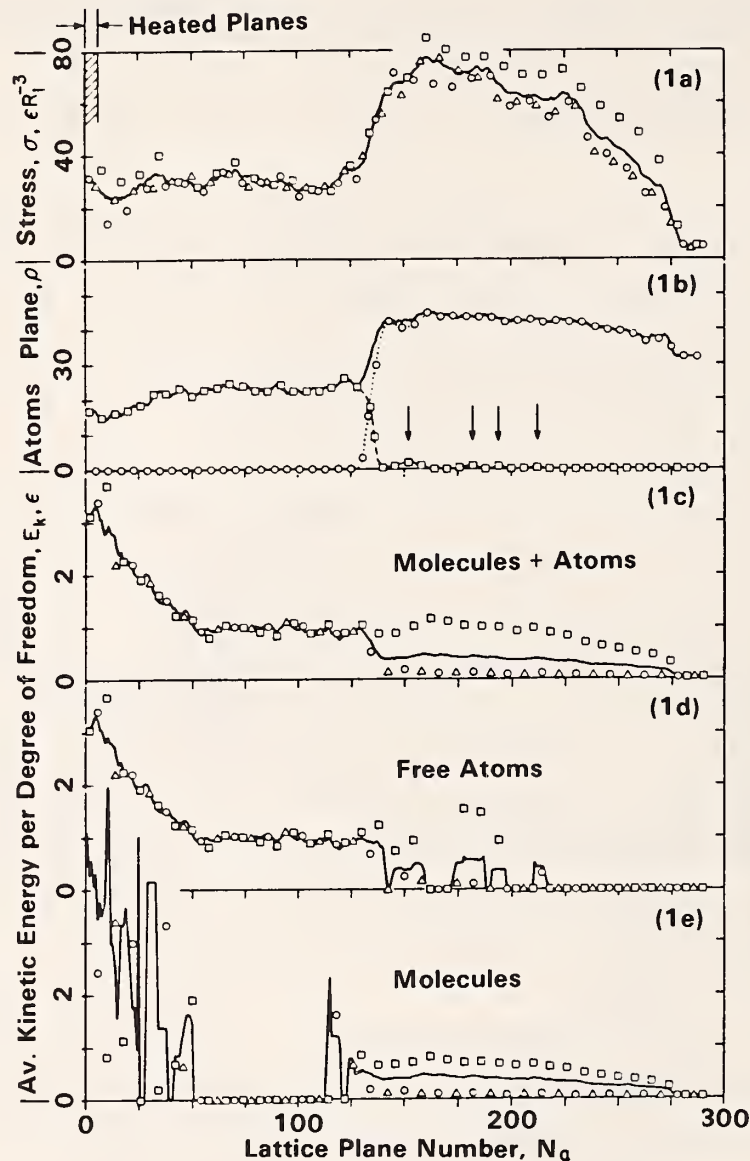


Figure 1. Profiles of the initiation of detonation at time step  $J=1800$ ,  $Q=32$ , as functions of distance from the mirror plane. Distance expressed in lattice plane number  $N_a$  of the undisturbed filament, spaced at  $0.5455 R_1$  between neighboring planes. (1a) Average of normal stress components  $\sigma$  (heavy curve) and individual X (o), Y ( $\Delta$ ), Z ( $\square$ ) components. (1b) Total number of atoms per plane  $\rho$  (heavy curve), the number of dissociated (o) and associated (o) atoms per plane. (1c) Average kinetic energy per degree of freedom  $E_k$  (heavy curve) of the molecules and dissociated atoms, and kinetic energies associated with velocities X (o), Y ( $\Delta$ ), Z ( $\square$ ) directions. (1d) Same as (1c) but of dissociated atoms only. (1e) Same as (1c) but of associated molecules only, in R (o), V ( $\Delta$ ) and T ( $\square$ ) degrees of freedom. Data have been smoothed by averaging over  $\pm 2$  neighboring planes ( $\pm 4$  for stress components in (1a)) and over 30 time steps.



with those discussed by, for example, Nesbitt and Hynes<sup>4</sup> who studied the theory of vibrational relaxation of  $I_2$  in liquid  $CCl_4$ . Our results thus demonstrate the usefulness of the MD method for studying not only the dynamics of detonation, but also the more general problems of energy transport and energy sharing.

Our model was a hypothetical diatomic bcc crystal capable of undergoing dissociation:  $A_2 = A + A + \text{energy}$ , similar to that described in Ref. 5-6. The atoms were considered to be independent particles interacting with one another through a compound Morse potential  $V_1 - V_2$ :

$$\begin{aligned} V_1 &= \epsilon \{ \exp[-2a_1(R-R_1)] - 2\exp[-a_1(R-R_1)] \}, \text{ for } R \geq R_{\text{dis}}; \\ V_2 &= b_2 \epsilon \{ \exp[-2a_2(R-0.15R_1)] \\ &\quad - 2\exp[-a_2(R-0.15R_1)] \} + Q\epsilon, \text{ for } R < R_{\text{dis}}. \end{aligned}$$

Here  $R = R_{ij}$  is the separation distance between atoms  $i$  and  $j$ ,  $\epsilon$  is the unit of energy,  $R_1 = 1.0$  is the unit of length,  $a_1 = \ln 2/0.255$ ,  $a_2 = \ln 2/0.05$ ,  $b_2 = 0.4$ , and  $Q$ , the exothermicity parameter, is 32. With these values,  $V_1 = V_2$  at  $R_{\text{dis}} = 0.2983$ . When  $R_{ij} < R_{\text{dis}}$ , atom  $i$  forms a molecule with atom  $j$  and interacts with  $j$  through  $V_2$ . Once formed, bond  $ij$  is saturated, such that other neighbors  $k$  of atom  $i$  interact with  $i$  through  $V_1$ . When  $R_{ij} \geq R_{\text{dis}}$ , molecule  $ij$  is dissociated,  $i$  and  $j$  now interact also through  $V_1$ . The atomic mass  $m$  was taken to be unity and the unit of time  $\tau$  to be  $R_1(m/\epsilon)^{1/2}$ . In Ref. 5-6, we showed that the kinetic and energy sharing properties of this simple model were reasonably realistic. At the high temperatures involved here, quantum mechanical effects should be small.

In earlier work,<sup>7</sup> we have investigated the energy propagation and energy relaxation in a filament of a three-dimensional monatomic crystal and monatomic dense liquid, subjected to shock compression and to pulsed heating. We combine the schemes developed in Ref. 5-7 for this study. To save computation, we built up the filament by joining together cubic blocks of crystallites each containing 128 molecules (256 atoms,  $4 \times 4 \times 4$  unit cells) and having periodic boundaries on opposite faces. The coordinate axes were aligned with the crystalline axes, the longitudinal direction  $Z$  being the direction of propagation of detonation. The boundary at  $Z = 0$  was a stationary mirror plane. Before starting, the system was equilibrated in its molecular form at a low temperature. The initial kinetic energy of the filament was set at  $E_k \approx 0.26\epsilon$ , just below the threshold of spontaneous dissociation (cf. Ref. 5). Then the first six crystalline planes were rapidly heated to a higher temperature. The heating was effected by scaling the velocities of the atoms in these planes by a factor 1.03526 per time step for 80 time steps. After heating, the system was allowed to evolve without further adjustment. The heating initiated dissociation



reactions which caused further reactions to occur along the filament by thermal conduction. The longitudinal expansion of the filament due to the initial heating and due to the dissociation drove a strong shock wave into the filament. Between the mirror plane and the shock front, the periodic boundary condition in the Z direction did not apply. But beyond the shock front, the filament was not yet disturbed, so that it could be joined smoothly to a single block of crystallite still at equilibrium, through the periodic boundary condition in the Z direction. This single block thus served to terminate the computation at a given time step. As time increased, we moved this block along, always keeping it ahead of the shock front. The computation continued to a maximum of 2210 time steps with the shock front reaching 335 lattice planes from the mirror plane. At this point the filament contained over 11000 atoms. The total energy of the system was monitored and found to be well conserved. From the dynamics of all the particles as a function of time, we then obtained a description of the initiation of detonation on a molecular scale.

Figures 1a to 1e show a typical set of results (single case-history) with  $Q = 32$  at time step  $J = 1800$  ( $\tau = 18$ ,  $\Delta\tau = 0.01$ , longitudinal sound velocity = 9.4 lattice planes per unit  $\tau$ ). Figure 1a gives the average of the normal stress components  $\sigma$ . Figure 1b gives the number of atoms per plane  $\rho$ . Figure 1c shows the average kinetic energy of the atoms  $E_k$  per degree of freedom. In these figures the shock front was at  $N_a = 280$ , and through the shock front  $\sigma$ ,  $\rho$ , and  $E_k$  increased abruptly. Between  $N_a = 275$  and  $N_a = 140$ , these quantities increased more slowly, reaching a peak around  $N_a = 160$ . In this region of shock compression there was also partial dissociation initiated at random sites (arrows in Figure 1b) after certain induction time had elapsed. But the main reaction occurred between  $N_a = 140$  and  $N_a = 125$ , where the dissociation proceeded rapidly to completion. This was accompanied by a sharp drop in  $\sigma$  and  $\rho$  and a sharp rise in  $E_k$ . Between  $N_a = 125$  and  $N_a = 50$ , the components of the normal stresses and the kinetic energy (Figures 1a and 1c) have equilibrated. The higher values of  $E_k$  and the lower values of  $\rho$  for  $N_a < 50$  resulted from the initial heating of the first six planes.

Returning to the region of shock compression, we conclude from the persistent difference between  $\sigma_z$  and  $\sigma_x$ ,  $\sigma_y$  and between  $E_{kz}$  and  $E_{kx}$ ,  $E_{ky}$  that there was mass motion in the Z direction in this region. This was clearly due to the thermal expansion and the volume change  $\Delta V$  (Reference 6) of the reacted region between the mirror plane and  $N_a = 125$ . From the positions of the shock front at different times it was possible to determine that the velocity of the shock front, as well as the

average peak stress, etc., had become very nearly steady after  $\tau = 14$ . The Mach number of the nearly steady shock front was just under 1.5.

The reaction front (at  $N_a = 140$ ) propagated more slowly than the shock front, so that the disturbance from the reaction was greater nearer the reaction front. This was responsible for the gradual decrease of the stress profile toward the shock front. We shall return to this point concerning the lower velocity of the reaction front. But we note that the random reaction sites also contributed to raising the local kinetic energy and the local stresses, and thus to the gradual decrease of  $\sigma$ ,  $\rho$ , and  $E_k$  profiles toward the shock front. Except for the gradual decrease of these quantities, our results are qualitatively similar to the continuum results described in Figure 11.9-2 of Ref. 2 for a steady detonation wave in a perfect gas.

Figure 1d shows the average kinetic energy of the dissociated free atoms per degree of freedom. The various sites of reaction between  $N_a = 215$  and  $N_a = 145$  correspond to the arrows in Figure 1b. The disturbance was quite large and undoubtedly generated stress pulses also in the transverse direction. These reaction sites tended to grow in size with passage of time (e.g., at  $N_a = 150$ , Figure 1b). They also moved with a mass average velocity as the filament expanded in the Z direction. These features may be responsible for the development of the cellular structure observed in detonation wave experiments (Chapter 7, Reference 1), but further studies will be needed to establish the connection.

Figure 1e is a plot of the average kinetic energy per degree of freedom of the associated atoms. The data show clearly that the energy transfer between the shock compression and the internal degrees of freedom was highly inefficient, in qualitative agreement with the ideas advanced by Pastine et al. There was no thermal equilibrium in the shock compressed region. Near the mirror plane, there were a few recombined molecules.

From profiles such as those in Figure 1b at different times, we could also determine the velocity of propagation of the reaction front. In the present case, this velocity was definitely lower than the velocity of the shock front, so that the wave profile as a whole was not steady. With the stationary mirror plane as a boundary condition, our problem corresponded to the special case of zero piston velocity in the "piston problem" discussed by Fickett and Davis.<sup>8</sup> We could simulate the case of an "overdriven" detonation wave by giving the filament a uniform mass average velocity toward the mirror plane and determine the condition that would give rise to a steady detonation wave. This investigation is now in progress.

The energy released at the reaction front drives the shock wave which converts the energy of reaction to the energy of compression. When both the reaction front and the shock front have steady velocities (not necessarily equal velocities), as appeared to be the case here, we could determine the energy of reaction by "measuring" the rate of energy propagation under the shock wave. For the present case, the average energy released by the molecular dissociation was 12.22e per atom. Our limited data for  $Q = 16$  and  $Q = 24$  appear to show a steadily weakening shock wave, perhaps leading to extinction of the reaction.

In conclusion, our results show that the initiation of detonation may be studied on a molecular scale by the MD method. This method is capable of providing many details, such as those involving energy transfer and energy relaxation. But our work is clearly just the beginning and many important and difficult problems remain to be studied. Among these are the problems of obtaining adequate data for ensemble averaging, the development of a steady overdriven detonation wave, the limit of detonation, a more realistic model of a molecular crystal, the role of defects and others.

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## ADVANCED NEUTRON METHODS

N. Berk, D. Fravel, C. Glinka, J. LaRock, and J. M. Rowe

## 1. Small Angle Neutron Scattering (SANS)

The SANS spectrometer was fully utilized during the past year with demand for instrument time exceeding available capacity by roughly 25 percent. During this period of heavy utilization, no major modifications were made to the facility, however, a number of minor improvements were carried out in order to improve its efficient use. For example, a new six-position, computer controlled, specimen changer was built primarily for solution scattering experiments. The holder can be used in air or under vacuum and is equipped with cooling coils and individual resistance heaters for maintaining samples at temperatures between 0-80°C. Also now available for room temperature measurements in magnetic fields up to 13 Kgauss is a four-position automatic sample changer (designed and built by G. R. Odette et al., University of California at Santa Barbara), which translates samples between the pole pieces of a vertical field electromagnet. For low temperature measurements in a magnetic field, the sample support of a controlled temperature cryostat has been modified to fit between the pole faces of a large horizontal field electromagnet thus enabling data to be taken at temperatures down to 4K in fields up to 15 Kgauss.

To reduce the time required to put SANS data on an absolute cross section scale, the strong scattering from a sealed 1 mm thick sample of microporous silica particles (pore diameter ~9 nm) has been calibrated against the incoherent scattering of pure vanadium. The forward scattering from this silica sample can be precisely determined in as little as one-half hour in many cases and is now routinely used as a secondary absolute intensity standard.

A detailed Users' Manual has been written to serve as both an introduction to the facility for new users as well as a reference manual for experienced users. In addition, nearly all of the SANS data reduction software is now documented and stored on the VAX computer and can be accessed by a user at a video terminal as needed. Data analysis software continues to be developed or adapted for use within the existing data reduction environment. For example, programs have been developed (by N. Berk) for the analysis of beam broadening by micron sized inhomogenieties or particles. Programs for desmearing SANS data from systems of randomly oriented identical particles (provided by V. Ramakrishnan, ORNL) and for extracting particle size distributions (provided by R. Page, Southwest Research Institute) are also now available.



## REACTOR RADIATION DIVISION AND COLLABORATIVE PROGRAMS

In order to improve the instrument's signal-to-noise ratio, tests have been made of a new detector fill gas mixture of  $^3\text{He}/\text{CF}_4$  using the facility's backup 25 x 25 cm<sup>2</sup> area detector. This gas mixture has been reported<sup>1</sup> to be far less sensitive to gamma rays than the  $^3\text{He}/\text{Xe}$  mixture presently used. Our test measurements confirm these reports and indicate that an 80% reduction in the gamma ray contribution to the background is possible with the new fill gas. Consequently, the instrument's primary, 65 x 65 cm<sup>2</sup>, detector will be refilled during the Summer 1984 reactor shutdown. The doubling of the reactor power which will take place during this shutdown, together with the new detector fill gas, should improve the signal-to-noise ratio for weak scattering samples by factors of between two to five.

In the past year, approximately fifty scientists representing six NBS divisions, ten universities and nine industrial and government laboratories have carried out experiments in polymers, ceramics, metallurgy, magnetism and biology using the SANS facility. Much of the recent work in polymers has concentrated on examining the density fluctuations which develop in polymer blends and block copolymer melts near their miscibility gaps or microphase separation boundaries, respectively. For example, C. Han of the Polymer Division along with collaborators from the University of Massachusetts have studied the critical density fluctuations in blends of deuterated polystyrene and polyvinyl methyl ether (PVME) as a function of temperature and PVME volume fraction. While they find that the correlation range of these fluctuations varies with temperature as predicted by mean field theory, they have also observed, in contradiction to traditional theory, that the blend interaction parameter  $\chi$  is strongly dependent on the relative volume fraction of the polymers. A strong dependence on volume fraction for  $\chi$  has also been found by F. Bates (AT&T Bell Laboratories) in measurements on block copolymers of 1,4-deutero-polybutadiene and 1,2-polybutadiene near their microphase separation conditions. These recent experiments by Han and Bates have provided some of the most detailed data to date on the actual functional dependence of  $\chi$ .

In their initial studies of epoxy thermosets, W. Wu and B. Bauer of the Polymer Division have been able, using deuterium labeling techniques, to observe the formation of paracrystalline-like networks in the solidified state. Furthermore, by carefully varying the sample temperature in-situ, they have been able to follow the network formation in real time.

In ceramics, the beam broadening produced by ceramic powders and compacts is being studied experimentally by K. Hardman-Rhyne of the Inorganic Materials Division and theoretically by N. F. Berk. Recent work has focused on determining the particle

size in alumina powders and the pore size in compacts prepared from such powders. The analysis of such data entails complex, numerical, multiple scattering calculations which include both the refractive and diffractive terms in the single particle scattering. In related studies of pore accessibility in microporous materials, contrast variation experiments using both polar and nonpolar solvents have been carried out on coals by J. Gethner of Exxon Research Co. and on silica particles used in liquid chromatography by L. Sander of the Organic Analytical Research Division and C. Glinka.

A number of recent experiments in metallurgy have been concerned with the microstructure of steels. M. Fatemi of the Naval Research Laboratory, for example, has been measuring the size distribution and volume fraction of precipitates in certain high strength, low alloy steels of interest to the Navy. G. R. Odette of the University of California at Santa Barbara has been interested in the effects of irradiation on reactor pressure vessel steels. In his SANS experiments he has observed dramatic, radiation enhanced, precipitation of copper impurities which leads to hardening and eventual embrittlement of the steel. R. Fields of the Fracture and Deformation Division and B. Mozer have studied creep cavitation in stainless steel and most recently in pure copper.

SANS studies of spin glass magnetic ordering in a number of amorphous rare earth-transition metal alloys have been carried out by J. Rhyne along with M. Spano of the Naval Surface Weapons Center and S. Pickart of the University of Rhode Island. They have shown that spin glass ordering, rather than long range ferro- or ferrimagnetic order, persists in these alloys at low temperatures even for very low rare earth element concentrations (e.g. in  $\text{Fe}_{.98}\text{Tb}_{.02}$ ) due to the random single-ion anisotropy field introduced by the rare earth atoms.

Some of the work mentioned above is described in greater detail in other articles in this report.

DETERMINATION OF PORE ACCESSIBILITY IN SILICA CHROMATOGRAPHIC PARTICLES  
BY SMALL ANGLE NEUTRON SCATTERINGLane Sander  
(Organic Analytical Research Division)

and

C. J. Glinka

We have been using small angle neutron scattering (SANS) to characterize the size, surface area and volume fraction of micropores in silica particles used in size exclusion liquid chromatography.<sup>1</sup> Recently these measurements have been extended to silica samples which have been saturated in solutions of  $H_2O/D_2O$  in order to determine the extent to which the pores are accessible to solvents. This question is relevant to the performance of this material for chemical separation in liquid chromatography.

Figure 1 shows the small angle scattering observed from a commercial silica powder consisting of 6.5 micron particles whose pores are nominally 30 nm in diameter. The dashed curve is the scattering from a dry silica sample while the solid curve is the scattering measured after saturating the silica with a solution of 59%  $D_2O$ , 41%  $H_2O$ . This  $H_2O/D_2O$  mixture is calculated to have the same scattering length density as silica assuming a skeletal density of 2.21 gm/cc. The scattering from the saturated sample is reduced a thousandfold from that of the dry sample at the smallest Q value measured (the Q-independent scattering at larger Q is due to incoherent scattering from the  $H_2O$  in the solution) suggesting that virtually all of the pores are accessible to the solution. This inference was confirmed by making measurements as a function of the  $H_2O/D_2O$  ratio in the saturating solution. These results are summarized in Figure 2 in which the square root of the scattering above background at the smallest Q measured is plotted versus the percentage of  $H_2O$  in the solution. This quantity should be simply proportional to the scattering contrast between the silica and the solution if all of the pores are filled. The linear dependence seen in Figure 2 demonstrates that this is the case and implies that a 39.5%  $H_2O$  solution would completely mask all of the pore scattering. Measurements of this type are now being extended to smaller pore materials.

The ability to completely mask the strong scattering from the porous structure of silica particles suggests that SANS would be a powerful technique for the study of absorbed phases on these high surface area materials. For example, it should be possible to determine the conformation of polymer chains chemisorbed to the pore surfaces. Such "bonded phase" materials are used in chromatography and SANS data



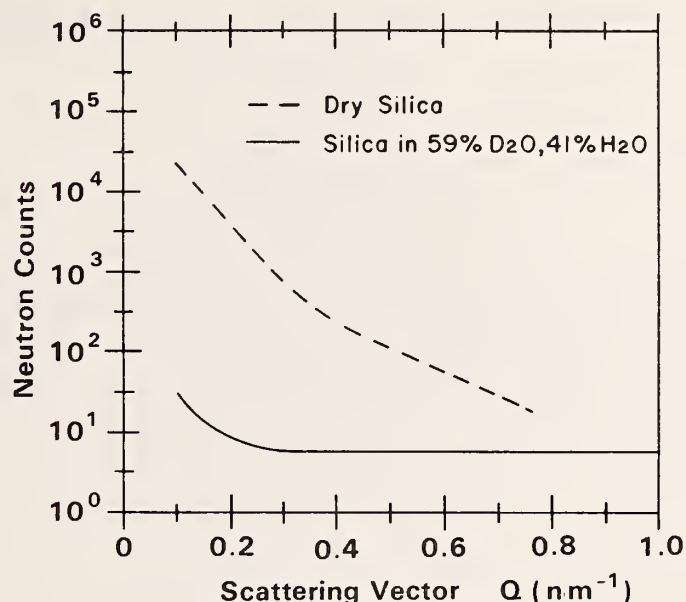


Figure 1. Comparison of the small angle scattering from microporous silica particles before and after saturating the particles in a 59%  $D_2O$ /41%  $H_2O$  solution. The water mixture has nearly the same scattering length density as the silica and thus masks the scattering from filled pores.

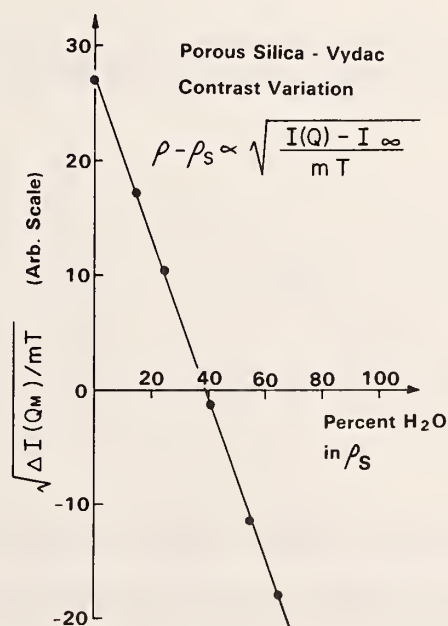


Figure 2. Plotted is the square root of the net scattered intensity (at  $Q = 0.1 \text{ nm}^{-1}$ ) from microporous silica particles saturated in  $H_2O/D_2O$  mixtures of various concentrations. The observed linear dependence indicates that the solutions fill the pores uniformly.

may, therefore, contribute to an understanding of their chemical selectivity. Experiments along these lines are planned for the near future.



## ANALYSIS OF BEAM BROADENING SANS DATA FROM ALUMINA POWDER

N. F. Berk

and

K. Hardman-Rhyne  
(Inorganic Materials Division)

We are continuing the work begun in the previous report period of developing a practical theory for incoherent small angle neutron multiple scattering that takes account of the general phase shift dependence of the single (spherical) particle neutron scattering cross-section. This approach gives us a tool for analyzing small angle neutron scattering data from ceramic and other materials and determining particle or void size from data that is dominated by multiple scattering. An important new example of the method is illustrated by Figure 1. Alumina powder of well-characterized, approximately monodisperse particle size was measured at several neutron wavelengths, volume fractions, and sample thicknesses, and the beam broadening data were fit with the theory, refining only on the particle size. The result, particle radius  $R = .265$  microns, is in good agreement with other estimates.

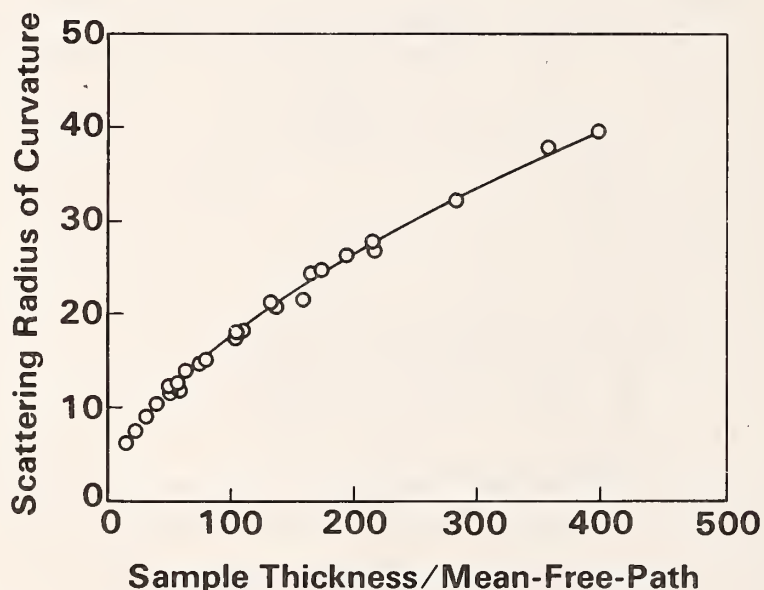


Figure 1. Collated alumina data (circles) and theoretical curve (line). The abscissa is the radius of curvature,  $r_c$ , of the beam broadened neutron scattering intensity in units of  $QR$ , where  $R$  was determined by best fit. Increasing  $r_c$  means increasing broadening. The ordinate is the "scattering power", i.e. sample thickness in units of the scattering mean-free-path length. The collated data lie on a universal curve for small angle multiple diffraction.

These particular data are described by multiple scattering in which the single particle cross-section is well approximated by the diffractive limit (phase shifts in the range 0.1-0.3) but where the mean-free-path is nevertheless small compared with sample size. This multiple diffraction is observable because of the relatively high density of scattering particles (volume fraction about 0.3) and the large values of sample thicknesses (2-10 mm). The figure shows all the data on a single graph in which the ordinate is the radius of curvature of the scattering curves at  $Q = 0$ --essentially a measure of the width of the beam broadening--in dimensionless units of  $QR$  (unbroadened single particle scattering corresponds to an ordinate of value 1.6 in this method of presentation), and where the abscissa is the computed ratio of sample thickness to scattering mean-free-path. The solid line is the theoretical determination of the scattering radius of curvature. Thus, when the scattering particle radius has been determined, the observed beam width is completely characterized by the properly normalized sample thickness, and all data (from monodisperse spheres) lie on the same curve. This may be taken to be the signature of small angle multiple diffraction.

#### THEORY OF INCOHERENT MULTIPLE SMALL ANGLE NEUTRON SCATTERING: PHASE SHIFT DEPENDENCE OF THE SINGLE PARTICLE SCATTERING

N. F. Berk

Work is continuing on the development of a practical theory of incoherent small angle neutron multiple scattering that incorporates the complete phase shift dependence of the single (spherical) particle neutron scattering cross-section. A recent application of the approach to beam broadening SANS data from alumina powder is given elsewhere in this Summary of Activities (N. F. Berk and K. Hardman-Rhyne). The phase shift dependence of the single particle scattering cross-section has also been examined in new detail. Among the results:

(1) The Porod law is independent of the phase shift,  $\rho$ , but its observability decreases with increasing phase shift (i.e., pushed to larger scattering angle); the observable asymptotic behavior may also appear to be Porod-like but strongly dependent on  $\rho$ .

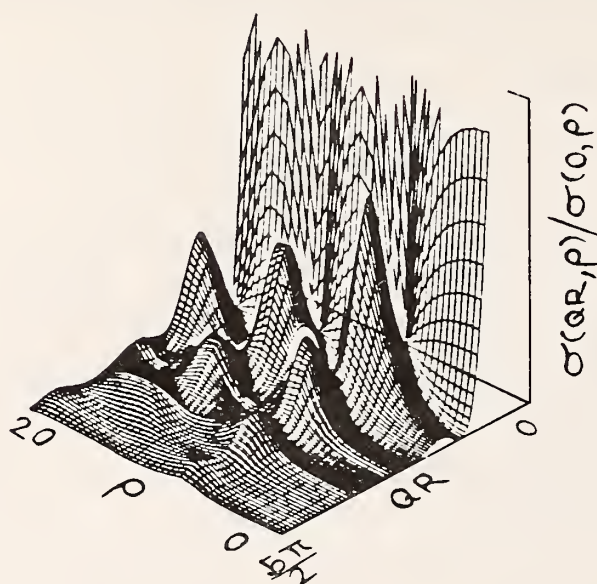


Figure 1. Single particle scattering cross-section of a sphere,  $\sigma(QR, \rho)$ . The diffraction limit (Born approximation) lies along the front edge,  $\rho = 0$ . The first big peak occurs near  $\rho = 7$ .

(2) The Born approximation for single particle scattering, which defines the diffraction limit for  $\rho \rightarrow 0$ , remains a very good approximation for  $\rho \leq 2.0$ . For  $\rho > 3.0$ , deviations from the diffraction limit become significant, and the oscillatory structure at  $QR > 1.0$  is strongly amplified. This is illustrated in Figure 1, which shows the single particle cross-section  $\sigma(QR, \rho)$  over a range of  $QR$  and  $\rho$ . The classical refractive (ray optical) limit, corresponding to  $\rho \rightarrow \infty$ , may not be observable in practice.

These findings have implications for the interpretation of SANS data from large particles, the inversion of SANS data to find particle size distributions, the information content of SANS data under conditions of low wavelength resolution, and other aspects of SANS analysis, even in the absence of strong multiple scattering.



SMALL ANGLE NEUTRON DIFFRACTION MEASUREMENTS OF DIBLOCK COPOLYMER PSD-PMMA  
IN THE BULK AND IN SOLUTION NEAR THE  $\theta$  POINTH. Benoit<sup>+</sup>, B. Bauer, and W. Wu  
(Polymer Division)

and

B. Mozer

Bulk samples of the copolymer prepared from deuterated polystyrene (PSD) and polymethylmethacrylate (PMMA) were obtained from anionic polymerization and formed in a brass vacuum mold. The molding process resulted in bulk samples free of any gas bubbles as analyzed by small angle x-ray diffraction. The characteristics of the copolymer were 43% PSD and 57% PMMA with  $Mn_1$  (DPS) = 83,000,  $n_1 = 741$ ,  $Mn_2 = 110,000$ ,  $n_2 = 1100$  leading to a ratio of  $Mw_1/Mn_1 = Mw_2/Mn_2 = 1.25$ . The solution sample was prepared in cyclohexanol, a known solvent for PSD, PMMA and their copolymer. The theta temperatures for both polymers are fairly close to each other which will lead to simplifications in the analysis of the neutron data. The solution was 20% by weight of the polymer in the cyclohexanol.

In order to determine the background and incoherent scattering from the solution, a mixture of low molecular weight liquids was prepared with the same ratio of atoms as in the 20% solution of 43% PSD content. This "background" mixture contained weight fraction of 0.700 cyclohexanol, 0.185 acetone, 0.086 benzene-d<sub>6</sub>, and 0.02% benzene.

Small angle neutron scattering (SANS) data were taken on the bulk sample at 20, 110, and 160°C, on the 20% solution at 76, 82, and 110°C, and on the "background" liquid mixture at room temperature. Background measurements, empty sample cell measurements, and transmission measurements were also made. The NBS-SANS spectrometer was employed in a configuration using the focused collimation system, the sample translation system, the area detector at 3.6 meters, the center of the detector at zero angle, and the incoming neutron beam of 5Å. Only one position of the sample translation system was used in order to fix precisely the position in the beam of the bulk, 20% solution, open beam, etc. measurements. There was no attempt to determine the absolute intensity of the scattering of our samples.

Transmission measurements of the mixed liquid and the 20% solution yielded the same value within one standard deviation of counting statistics. Thus, we have high confidence in the method for subtracting the contribution of any extraneous and incoherent scattering from the bulk or 20% solution scattering data.



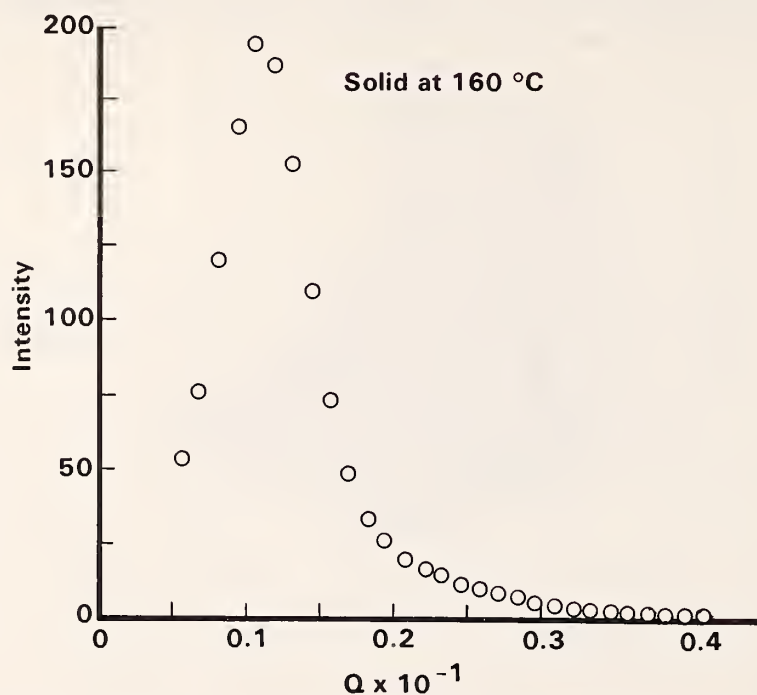


Figure 1. Corrected (SANS) intensity from bulk PSD-PMMA diblock copolymer at 160°C as a function of  $Q = 4\pi\sin\theta/\lambda$ .

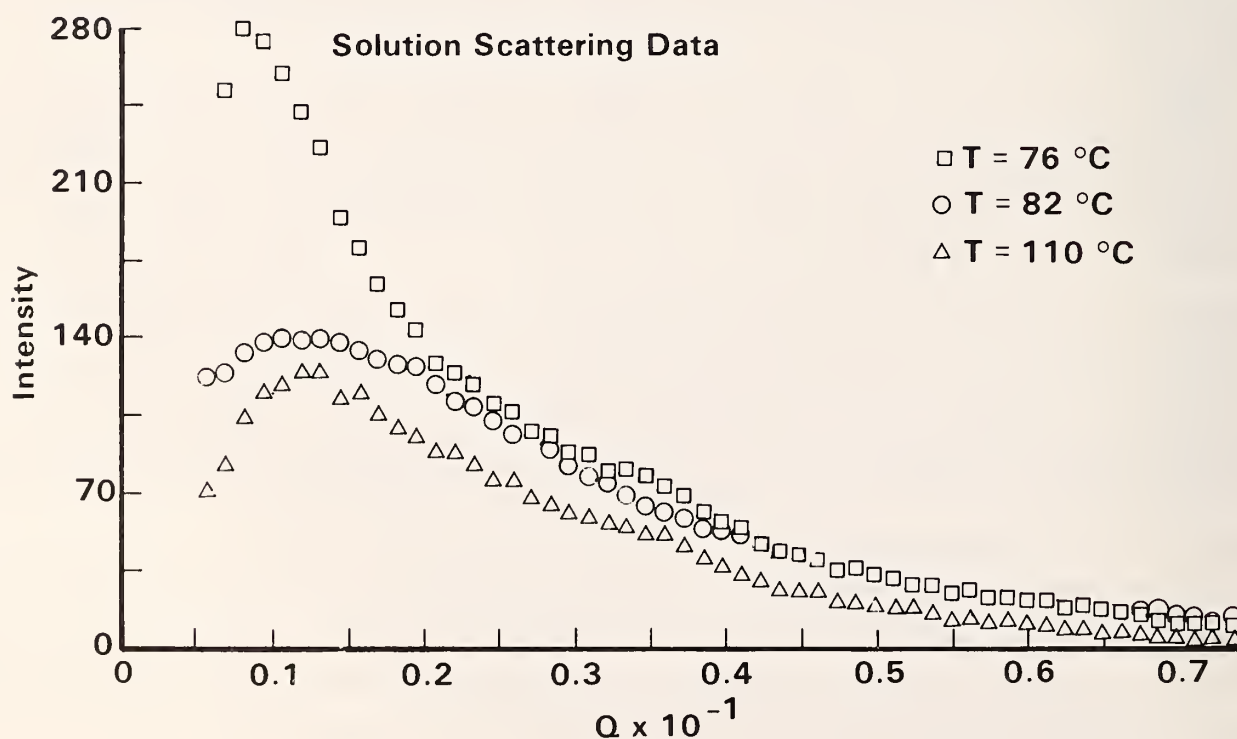


Figure 2. Corrected (SANS) intensity from a 20% solution of PSD-PMMA diblock copolymer in cyclohexanol at 76, 82, and 110°C versus  $Q = 4\pi\sin\theta/\lambda$ .

The corrected scattering intensity is shown for the bulk sample at only one temperature in Figure 1. Our measurements of the bulk sample showed no significant change with temperature in terms of the overall scattering pattern. The intensity of the maximum observed was very strong so that no corrections were needed for background or incoherent scattering. We found that the specimen scatters so intensely that it is useful for aligning the beam stop for other experiments. The corrected intensity for the scattering from the 20% solution is shown in Figure 2. The most striking feature of these measurements is the appearance of a well defined peak. This feature remains as the temperature is lowered to near the  $\theta$  temperature for the copolymer. Also evident is the large increase in intensity as the  $\theta$  temperature is approached.

A theoretical calculation of the scattering intensity for multicomponent systems with special application to homopolymer mixtures and copolymers has been performed by H. Benoit and M. Benmouna and others. The calculation can account for the observed scattering intensity for the bulk sample. Using the experimental scattering intensity, it is possible to fix the parameter in the theory representing the interference cross term of the scattering between the two different monomers. The theoretical calculation for the intensity of the scattering for a 20% copolymer in solution shows also the surprising feature of a peak that increases in intensity as the  $\theta$  temperature is approached.

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# NETWORK STRUCTURE OF PARTIALLY DEUTERATED EPOXYS FROM NEUTRON SCATTERING

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The physical properties of epoxy networks have been extensively studied due to their great commercial importance. These studies are of macroscopic quantities. Very little is known of the nature of the network structure, however. To gain insight into the network structure, neutron scattering studies have been initiated.

A partially deuterated epoxy, the diglycidyl ether of Bisphenol A (DGEBA), was synthesized. Perdeuterated phenol and acetone were condensed to give perdeuterated Bisphenol A. It was then reacted with epichlorohydrin to give an epoxy with 14 deuterium atoms in a central position. The network was formed by reacting the DGEBA with di or triamines based on polypropylene oxide flexible chains.

The scattering was performed on the small angle facility and on the BT-6 diffractometer. Studies were made by varying the amine type, by swelling the samples with solvent in order to assess the homogeneity of the network, and by quenching the curing reaction at various stages, to gain insights to the network formation process.

The most striking result from neutron scattering is the observation of multiple peaks in these AMORPHOUS materials. Such peaks are believed to be a consequence of intranetwork correlation among the deuterated blocks. The short range (liquid-like) correlation can only give rise to part of the first scattering maximum. The higher order peaks provide a strong indication that the pair correlation within a network is more expanded than a Gaussian coil.

A theory of the scattered intensity from labeled networks has been developed to analyze the experimental data. Parameters relating to network size and heterogeneity can thus be deduced from the scattering curves. The initial results indicate that the networks are far from uniform.

# NEUTRON CLOUD POINTS AND CONCENTRATION FLUCTUATIONS OF POLYMER BLENDS

C. C. Han  
(Polymers Division)

and

H. Yang, M. Shibayama and R. S. Stein  
(University of Massachusetts, Amherst, MA)

The phase diagram of polymer blends is traditionally studied by the light scattering cloud point measurement. Transmitted or scattered light is normally used for this purpose, the intensity of which abruptly changes at the vicinity of the phase transition temperature. We have previously studied PSD/PVME blends<sup>1</sup> by this conventional light scattering technique and it was found that the lower critical solution temperature (LCST) is about 40°C higher than that for homogeneous polystyrene PSH/PVME. However, there is one disadvantage in the light scattering technique. Because of the long wavelength involved one may not be able to detect the onset of transition from a stable to a metastable phase. This may be important if the polydispersity of polymers affects the phase separation phenomena. Small angle x-ray (SAXS) or neutron scattering (SANS) techniques are alternative since they are associated with radiation having appreciably shorter wavelengths. SANS is appropriate for PSD/PVME blends to detect the "neutron cloud point" which is the onset of phase transition in this case. This is because the scattering contrast between PSD and PVME is appreciably high. Furthermore, this technique allows one to obtain information about molecular parameters, such as the Flory-Huggins interaction parameter ( $\chi$ ) and the correlation length ( $\xi$ ) in the miscible regions of the blend system.

In this paper, we explore the feasibility of the neutron cloud point measurements and discuss the critical concentration fluctuation of PSD/PVME blends.

## Experimental

The system investigated was a blend of deuterated polystyrene (PSD) and poly(vinyl methyl ether) (PVME). The characteristics of these components are listed in Table 1. Samples of SANS experiments were prepared by dissolving the components in toluene and casting them into films, followed by drying in vacuum for a week at 70°C and then for 24 hours at 110°C in order to remove the residual solvent. The dried samples were compression molded at 80°C into discs of 19 mm in diameter and 1.7 mm in thickness.



The experiments were performed using the SANS facility at the National Bureau of Standards, Gaithersburg, MD, which has a two-dimensional position sensitive detector. The incident beam was monochromatized by a velocity selector and had an average wavelength ( $\lambda$ ) of 6Å. A focusing collimation system was used to obtain the lower limit of the scattering vector ( $q$ ) of  $0.005\text{Å}^{-1}$ , where  $q = \frac{4\pi}{\lambda} \sin(\theta/2)$  and  $\theta$  is the scattering angle. The sample was mounted in a brass cell covered with copper shims of 0.025 mm thickness in order to enhance heat conductivity.

The scattered intensity was collected over the two-dimensional detector pixels ( $0.005\text{Å}^{-1} \leq q \leq 0.12\text{Å}^{-1}$ ) and the dark current intensity due to electronic noise and room background was subtracted. There is no need for further detector response correction in this case. Samples were heated at a rate of  $1^\circ\text{C}/\text{min}$  and total intensities were recorded as a function of temperature. Phase separation was characterized by an upturn in total scattered intensity with temperature increase as shown in Figure 1. The intersection of straight lines drawn through portions of the curve below and above the break was taken as the neutron cloud point.

The sample temperatures for both SANS and LS experiments were carefully calibrated in terms of a copper-constantan thermocouple.

The absolute intensity calibration was done using a dry silica gel sample as a secondary standard, which was calibrated in terms of a vanadium standard (2).

### Results and Discussion

The scattering function,  $I(q,T)$ , of a miscible polymer blend has been calculated by de Gennes (3) based on the "Random Phase Approximation". This can be written as

$$\frac{K}{I(q,T)} = \frac{1}{Y_A g_A(Y_A, q) \phi_A} + \frac{1}{Y_B g_B(Y_B, q) \phi_B} - 2\chi(\phi, T) \quad (1)$$

where  $Y_i$  is the reduced degree of polymerization with respect to the unit cell volume,  $K$  is a constant, depends on the scattering geometry and the scattering lengths of monomers,  $\phi$  is the volume fraction,  $\chi$  is the Flory-Huggins interaction parameter,  $g_N(Y_N, q)$  is the Debye scattering function. The polymer chains in the blend are assumed to remain Gaussian, and at small  $q$ , eq. (1) can be written as:

$$\frac{K}{I(q,T)} = 2[\chi_s(\phi) - \chi(\phi, T)] = \frac{q^2 b^2}{18} \frac{1}{\phi_A \phi_B} \quad (2)$$

where

$$b = [\phi_A \phi_B \left( \frac{b_A^2}{\phi_A} + \frac{b_B^2}{\phi_B} \right)]^{1/2} \quad (3)$$

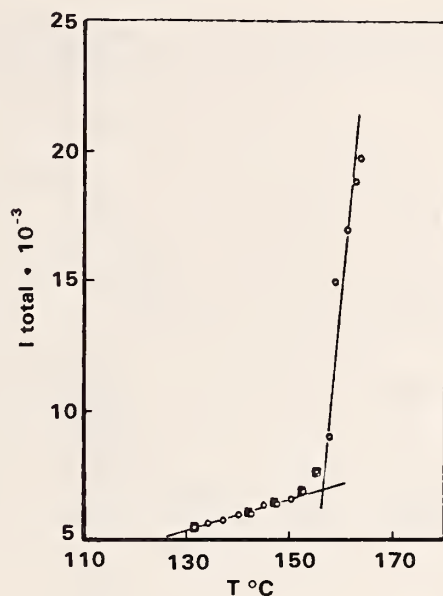


Figure 1. Experimental  $I_{\text{tot}}(T)$  (in open circle) and calculated  $I_{\text{tot}}(T)$  (in solid square) at various temperature for wt% 50/50 PSD/PVME blend. Solid lines are drawn through portions of experimental points to determine the neutron cloud point,  $T_{\text{cp}}^N$ .

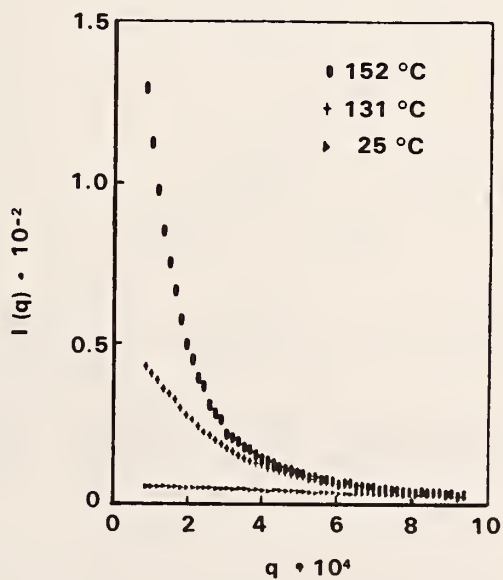


Figure 2. Scattered intensity as a function of  $q$  for the above blend at various temperatures.

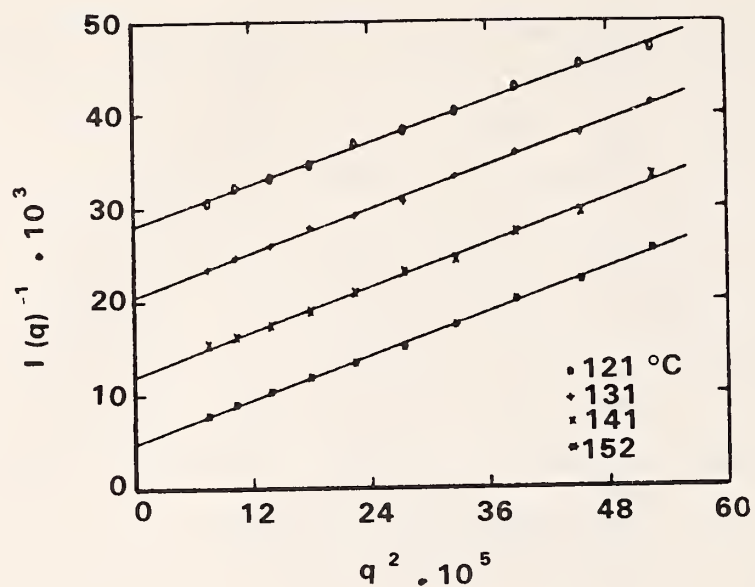


Figure 3. Inverse intensity vs  $q^2$  plots for the above blend at various temperatures.

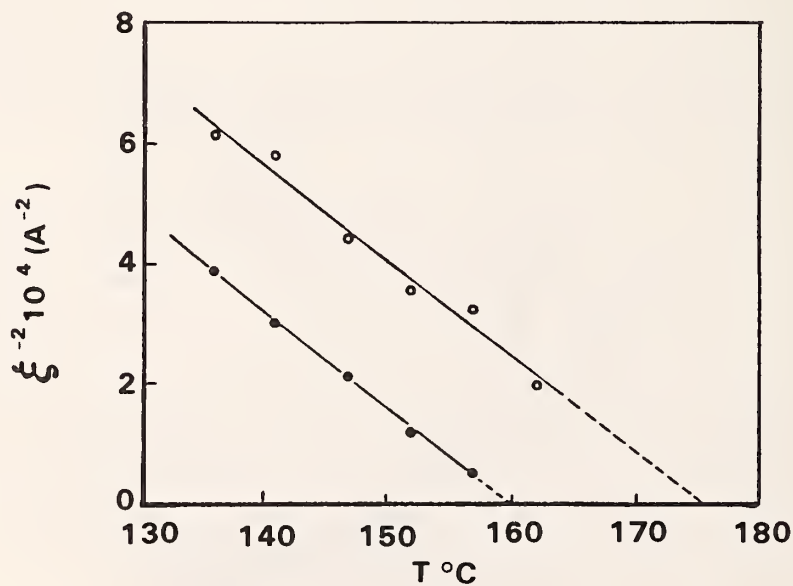


Figure 4. Inverse square correlation length,  $\xi^{-2}$  as a function of  $T$  for 50/50 (in solid circle) and 80/20 (in open circle) blends. Spinodal temperature is obtained at  $\xi^{-2} \rightarrow 0$ .

Table I. The characteristics of the blend component (PSD purchased from Polymer Laboratories, Stowe, OH and PVME for Scientific Polymer Products, Webster, NY).

| Component | $M_w$   | $M_w$  | $M_w/M_w$ |
|-----------|---------|--------|-----------|
| PSD       | 255,000 | --     | 1.08      |
| PVME      | 99,000  | 46,500 | 2.13      |

Table II. Correlation Length at Various Temperatures for Two Different Compositions

| PSD/PVME  | 50/50           | PSD/PVME  | 80/20          |
|-----------|-----------------|-----------|----------------|
| Temp (°C) | $\xi$ (Å)       | Temp (°C) | $\xi$ (Å)      |
| 121       | $36.5 \pm 0.5$  | 121       | $34.8 \pm 1.0$ |
| 131       | $43.6 \pm 0.6$  | 131       | $36.4 \pm 0.6$ |
| 136       | $50.6 \pm 1.2$  | 136       | $40.3 \pm 1.1$ |
| 141       | $57.4 \pm 1.2$  | 141       | $41.5 \pm 0.9$ |
| 147       | $68.2 \pm 1.2$  | 147       | $47.5 \pm 0.8$ |
| 152       | $90.6 \pm 2.2$  | 152       | $52.8 \pm 1.1$ |
| 157       | $135.6 \pm 4.8$ | 157       | $55.4 \pm 1.1$ |
|           |                 | 162       | $70.9 \pm 1.5$ |

 Table III. Calculated  $I_{tot}$  From Eq. (7) and Experimental  $I_{tot}$  for PSD/PVME 50/50

| Temp. | F ( $\xi$ ) | $I_{tot} 10^{-3}$ (calc) | $I_{tot} 10^{-3}$ (expt) |
|-------|-------------|--------------------------|--------------------------|
| 132   | 5.42        | 5.5*                     | 5.5*                     |
| 142   | 5.95        | 6.0                      | 6.1                      |
| 147   | 6.28        | 6.4                      | 6.4                      |
| 149   | 6.70        | 6.6                      | 6.7                      |
| 152   | 6.80        | 6.9                      | 6.9                      |
| 155   | 7.50        | 7.6                      | 7.6                      |

\*reference point

Table IV. The Neutron, Light Cloud Points and the Spinodal Temperatures for wt% 50/50 and 80/20 Blends

| Wt%   | $T_{cp}^L$ °C | $T_{cp}^N$ °C | $T_{sp}$ °C |
|-------|---------------|---------------|-------------|
| 50/50 | 157.0         | 156.0         | 160.0       |
| 80/20 | 171.0         | 168.5         | 176.0       |



and  $b_1$  is the statistical segment length of 1,  $\chi_s$  denotes the interaction parameter at the spinodal point. Eq. (2) can be written in a Lorentzian or Ornstein-Zernike form<sup>4</sup>

$$\frac{I(q,T)}{I(0,T)} = \frac{1}{1+q^2\xi(T)^2} \quad (4)$$

$$\text{with } \xi(T) = \frac{b}{6} \left\{ \phi_A \phi_B [\chi_s(\phi) - \chi(\phi,T)] \right\}^{-1/2} \quad (5)$$

This  $\xi(T)$  may be interpreted as the concentration correlation length at temperature  $T$ .

The scattering function of PSD/PVME with 50/50 weight percent is shown in Figure 2 for several different temperatures. Before we go into data analysis for correlation length, we would like to discuss the integrated intensity and cloud point study.

The total scattered intensity as a function of temperature in the miscible regions is experimentally determined by

$$I_{td}(T) \propto \int_{q_{min}}^{q_{max}} I(q,T) 2\pi q dq$$

which can be integrated to yield:

$$= 2\pi \frac{I(0,T)}{\xi^2(T)} \ln \left\{ \frac{\cos[\tan^{-1}(\xi q_{min})]}{\cos[\tan^{-1}(\xi q_{max})]} \right\} \quad (6)$$

where  $q_{min}$  and  $q_{max}$  are the lowest and highest limits of the scattering vector in our SANS geometry. From both eq. (2) and eq. (5)  $I(0,T)$  and  $\xi^2(T)$  terms can be cancelled out and lead eq. (7) to the following:

$$I_{tot}(T) \propto \ln \left\{ \frac{\cos[\tan^{-1}(\xi q_{min})]}{\cos[\tan^{-1}(\xi q_{max})]} \right\} = F(\xi) \quad (7)$$

The correlation length was obtained from the  $I(q,T)^{-1}$  vs.  $q^2$  plot as shown in Figure 3 according to eq. 4. The extracted  $\xi$ 's at various temperature are listed in Table II. It should be noted that the correlation length increases with increasing temperature. We can calculate  $I_{tot}(T)$  from the experimental correlation length by using eq. 7 as shown in Table III. By matching  $I_{tot}(T=132^\circ\text{C})$  as the reference point, it is clear that the data analysis schemes we have used so far are definitely consistent. The total intensity (counts) of scattered neutron before the onset of the phase separation has an insignificant increase.

From eq. (5) we know that  $\xi$  diverges at the spinodal point ( $T_s$ ). Recently, Schelten et al. used this correlation length approach to obtain the spinodal points ( $T_s$ ) and described the phenomena of critical fluctuations for PSD/PVME blends<sup>5</sup>. We have used the same technique to determine  $T_s$  which is shown in Figure 4. These

values together with the neutron cloud point  $T_{cp}^N$  are listed in Table IV. It is noted that the neutron cloud points are consistent with the light cloud points. Although the cloud points are lower than the corresponding spinodal points as we expected,  $T_s$  (160.0°C) for wt% 50/50 PSD/PVME sample is closer to the  $T_{cp}^N$  (156.0°C), but the  $T_s$  (176.0°C) for wt% 80/20 PSD/PVME sample is significantly higher than  $T_{cp}^N$  (168.5°C). This is because the critical composition for this LCST system is around 30% of PSD. The 80/20 sample is farther away from the critical composition. Further, studies of  $T_s$  from the correlation length approach, together with  $T_{cp}^N$  will be reported as a function of composition. The phenomena of critical fluctuations at various compositions as well as temperature and composition dependence of  $\chi$  for this particular system will also be discussed in the forthcoming paper<sup>6</sup>.

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NEUTRON SMALL ANGLE SCATTERING AND POLE FIGURE ANALYSIS  
OF CREPT COPPER SPECIMENS

Richard Fields  
(Fracture and Deformation Division)

and

Bernard Mozer  
(Reactor Radiation Division)

Small angle neutron scattering (SANS) measurements were taken on crept copper samples. The strained samples were copper rods given varying amounts of tensile creep at 600°C. Neutron scattering samples were prepared from these rods in several ways. One sample for each creep amount was cut so that the strain direction would be parallel to the incoming neutron beam. Another set of samples were cut so that the neutron beam was perpendicular to the strain direction. All these samples were polished so that they could also be used for metallurgical examinations. Rods not subjected to creep had samples prepared from them in the above manner to provide standards for comparison. All rods used were not cast material but mechanically formed and subjected to a 850°C anneal. The SANS spectrometer configuration used for this work consisted of a 27 mm hole for entrance collimation of the flight path and a 12 mm hole for exit collimation. Sample holders of cadmium were prepared with a 10 mm hole to define the beam and were used in the automatic sample changer. The detector was placed 3.6 meters from the sample at zero angle. Various wavelengths were used to cover the range of wave vector difference and to have good overlap from one wavelength to another so as to map out the scattering curve. Measurements were taken with the neutron beam parallel and perpendicular to the strain direction, on the respective standards, on the empty sample holder, the room background, and on the transmissions for the different wavelengths.

Data taken on the crept and standard samples for the 5Å neutrons showed an unusual effect where the scattering for the beam parallel to the strain axis was an order of magnitude larger than the scattering when the beam was perpendicular to the strain axis. This increased scattering disappeared when longer wavelength neutrons were used and it was concluded that we had observed double Bragg scattering from oriented samples caused by contamination of neutrons in the wavelength distribution which are not beyond the Bragg cut-off. As a consequence of this result, we decided to do pole figure diffraction analysis on the specimens to see orientational effects caused by creep. The results of the SANS measurements on two differently crept, minimum and maximum creep, samples are as follows. We observe isotropic scattering

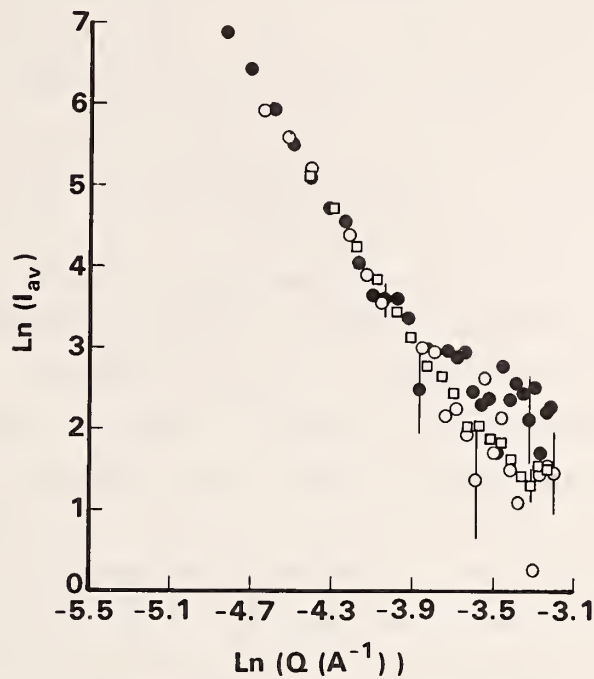


Figure 1. Summed scattering data from 6Å, 7.5Å, and 9Å impinging on a crept specimen versus  $Q = 4\pi\sin\theta/\lambda$ . For clarity we have used a log-log plot. The squares are 6Å data, the open circles 7.5Å data, and the closed circles are 9Å data.



Figure 2. A Pole Figure Plot of the data obtained for sample 4-C, the least crept sample, for reflections from the (111) planes.



from all specimens excluding the 5Å data. The most intensive scattering comes from the specimen which received the most creep. The intensity of the two standards is not zero but much less than the least crept specimen. There are differences in the scattering from the samples cut in different directions and the possibility exists that the scattering centers are structurally aligned. The data for three wavelengths, 6, 7.5, and 9Å, when summed so as to give the intensity versus  $Q = 4\pi\sin\theta/\lambda$ , can be normalized to one of them and the resulting curve in figure 1 shows nice overlap between the sets. The most striking feature of the experiment is that the functional form of the intensity is the same for all the specimens, crept or otherwise. The intensity varies as  $Q^{-N}$  representative of the Porod region or asymptotic region of the scattering curve.  $N$  is very close to 4 for any sample and lies between 4 and 5 if the scattering from the standard is subtracted from the scattering of the crept sample. It was not possible with the present configuration of the SANS spectrometer to see another part of the scattering curve, e.g., the Guinier region for small  $Q$ . Furthermore, it is necessary for us to do a calibration measurement on a standard sample to fix the absolute intensity of our data so as to obtain the surface to volume ratio using the Porod approximation.

Pole figure analysis of the least crept specimen was performed on BT-6' spectrometer using the 4-circle goniometer for rotation of the sample. Figure 2 shows the pole figure plot of the data for the (111) reflections. The intensity in the center is characteristic of fiber alignment along the strain direction. The other large intensity contours scattered in the ring about the center probably arise from the strain induced during production of the rod but not eliminated during the 850°C anneal.

Work is continuing on SANS and the pole figure diffraction measurements to complete our characterization of creep effects.

# NEUTRON DIFFRACTION STUDIES OF AMORPHOUS ALLOYS

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Neutron small angle scattering (SANS) and neutron diffraction (ND) measurements have been performed upon a number of amorphous alloy systems to characterize the structure of these alloys in the various states they traverse as a function of heat treatment which carries them from the amorphous state to the crystallographic state characteristic of the alloy in thermal equilibrium.

Metallic-glass ribbons of  $\text{Cu}_x\text{Ti}_{1-x}$  and  $\text{Cu}_x\text{Zr}_{1-x}$  were prepared by melt spinning the molten alloy onto a copper wheel in an argon atmosphere. Long metallic glass ribbons 2.0 mm wide and  $25 \times 10^{-3}$  mm thick can be prepared in this manner and show an absence of crystallinity when examined both by x-ray and neutron diffraction techniques. All heat treatment of the samples occurred with the sample contained in a sealed quartz tube which had been evacuated to high vacuum and then filled with an atmosphere of helium. Differential thermal analysis and transmission electron microscopy were performed on the samples at various heat treatments to have parallel characterization with the neutron measurements.

The most extensively studied sample was the  $\text{Cu}_{55}\text{Ti}_{45}$  alloy. Both SANS and ND data were taken in the as-cast condition, after an anneal of 300°C for 3 hours, 300°C for a total of 9 hours, 350°C for 1 hour, 403°C for 1 hour, 475°C for 2 1/4 hours, and 850°C for 20 hours. These temperatures are roughly below the glass transition, the glass transition, the crystallographic transition, and ultimately the thermal equilibrium state. Figure 1 shows SANS data characteristic of many of the alloys studied at various heat treatments. The data for the as-cast state and for the 300°C anneals is similar to the spectra at 350°C. One of the most striking features of the 350°C spectra and in the 850°C spectra is the non-isotropic pattern which persists throughout the heat treatment. Studies of other alloys showed that this pattern arises from oriented "precipitates" or particles of flat disk shape whose short dimension is oriented along the temperature gradient that exists when the alloy was

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quenched upon the spinning wheel. This pattern is observed in  $\text{Cu}_x\text{Ti}_{1-x}$  and  $\text{Cu}_x\text{Zr}_{1-x}$  alloys and we plan to investigate if it is common to all non-magnetic amorphous alloys. Its composition is unknown at the present time, but will be investigated with the scanning transmission electron microscope. One also notes the high isotropic scattering associated with a precipitating phase just at the crystallographic transition. With subsequent heat treatment, this isotropic scattering disappears probably with the growth and fusion of the fine particles with heat treatment whose dimension is too large to be observed in our spectrometer.

Figure 2 exhibits the ND patterns for the alloy in the amorphous state and in Figure 3 we see the patterns for the crystalline states, the non-equilibrium crystalline phases just after the transition, and its evolution to the equilibrium pattern after the two anneals. The sharp dip in the amorphous state that seems to give rise to the two main peaks (one peak has been called a precursor of chemical short range order by Sakata, Cowlam, and Davies<sup>1</sup>), we contend is caused by the negative scattering length of titanium and that titanium and copper in these amorphous systems are bound together in a molecular state giving rise to molecular

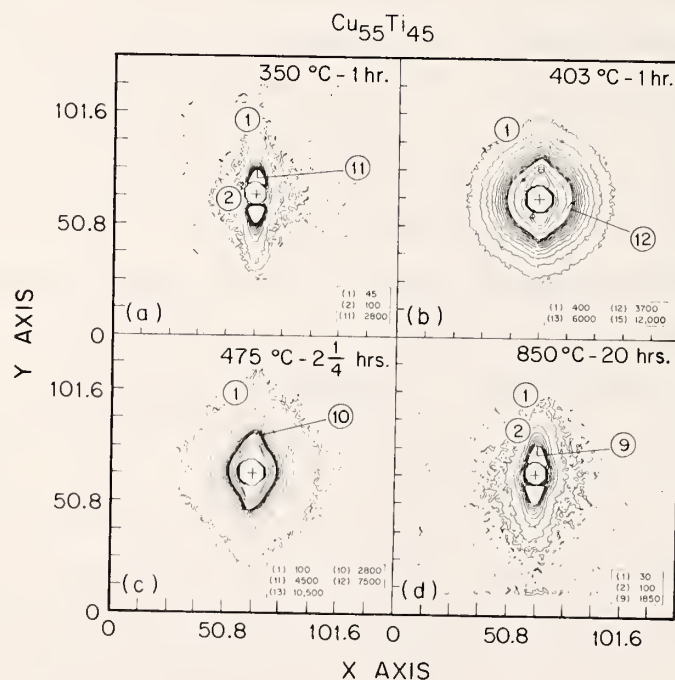


Figure 1. Topological intensity mapping of the small angle neutron scattering about the main neutron beam for an initial  $\text{Cu}_{55}\text{Ti}_{45}$  metallic glass after having the subsequent indicated thermal treatments. The axes indicate the detector position (via channel number) and the cross in the middle of each pattern indicates the center of the main beam. For each pattern, the intensities for the designated levels are given in the boxed insets. Between any two given levels the intensity varies linearly.

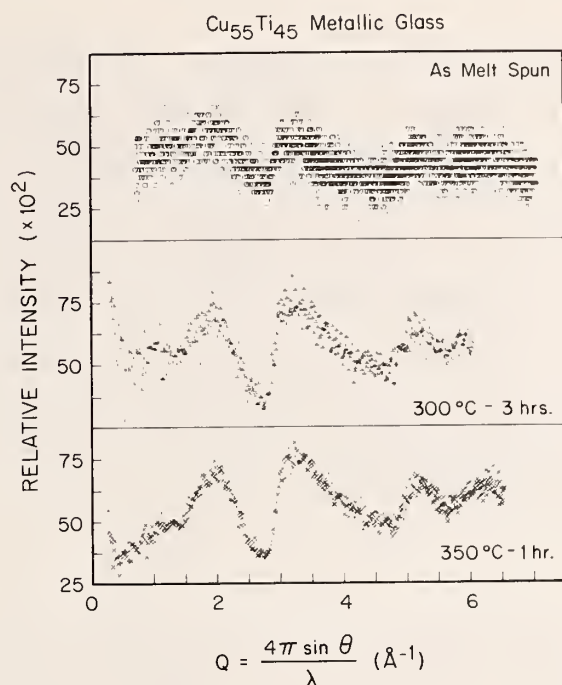


Figure 2. Relative Scattering Intensity (normalized to maximum intensity) vs. Scattering Vector,  $Q$ , for  $\text{Cu}_{55}\text{Ti}_{45}$  metallic glass heat treated at the indicated temperatures and times.

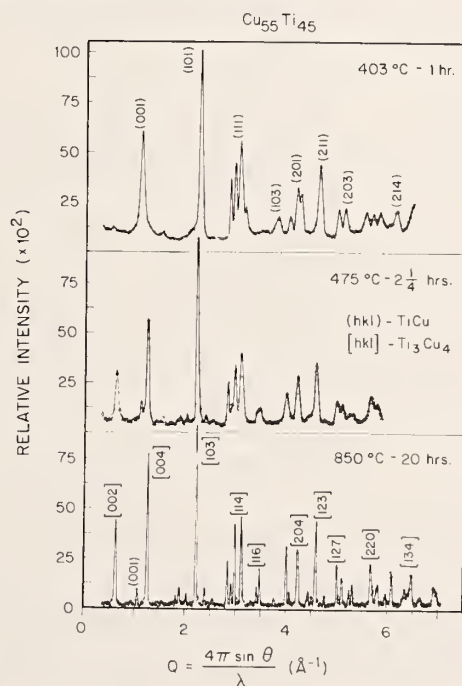


Figure 3. Relative scattering intensity normalized to maximum intensity of each pattern versus wave vector  $Q$  for the  $\text{Cu}_{55}\text{Ti}_{45}$  alloy just after crystallization, after heat treatment which does not produce equilibrium state, and high temperature treatment yielding equilibrium state.



amorphous systems and not atomic amorphous systems. The sharp dip is characteristic of a fixed length in the molecule and destructive interference because of the negative scattering length. We further contend that an alloy with positive scattering length isotope of titanium would show only a structure factor in the amorphous state similar to that of a simple atomic liquid or to that observed using x rays. One notes further that short range order peaks appear that eventually grow to Bragg peaks as the alloy is heated to the crystalline state. The crystalline pattern just after the transition appears to be that of a tetragonal TiCu (tP4) phase which disappears and is replaced by a pattern of mixed phases of TiCu and  $Ti_3Cu_4$  after subsequent heat treatment.

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### NEUTRON SCATTERING STUDIES OF THE MAGNETISM IN Cu-Mn SINGLE CRYSTALS

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We have carried out an extensive series of diffraction, inelastic, and small angle scattering experiments on  $Cu_{1-x}Mn_x$ , for  $x = 0.10, 0.15, 0.20$ , and  $0.25$ . This alloy system has historically been regarded as the prototype of spin glass behavior and has attracted considerable theoretical and experimental attention. Despite this level of activity, a satisfactory understanding of the origin of the magnetic properties of Cu-Mn, including the cusp in the magnetic susceptibility, has not yet become available. The discovery several years ago of the existence of incommensurate magnetic peaks<sup>1</sup> has led us to these new experiments and a new view of the origin of magnetism in Cu-Mn. The incommensurate magnetic peaks occur at the positions

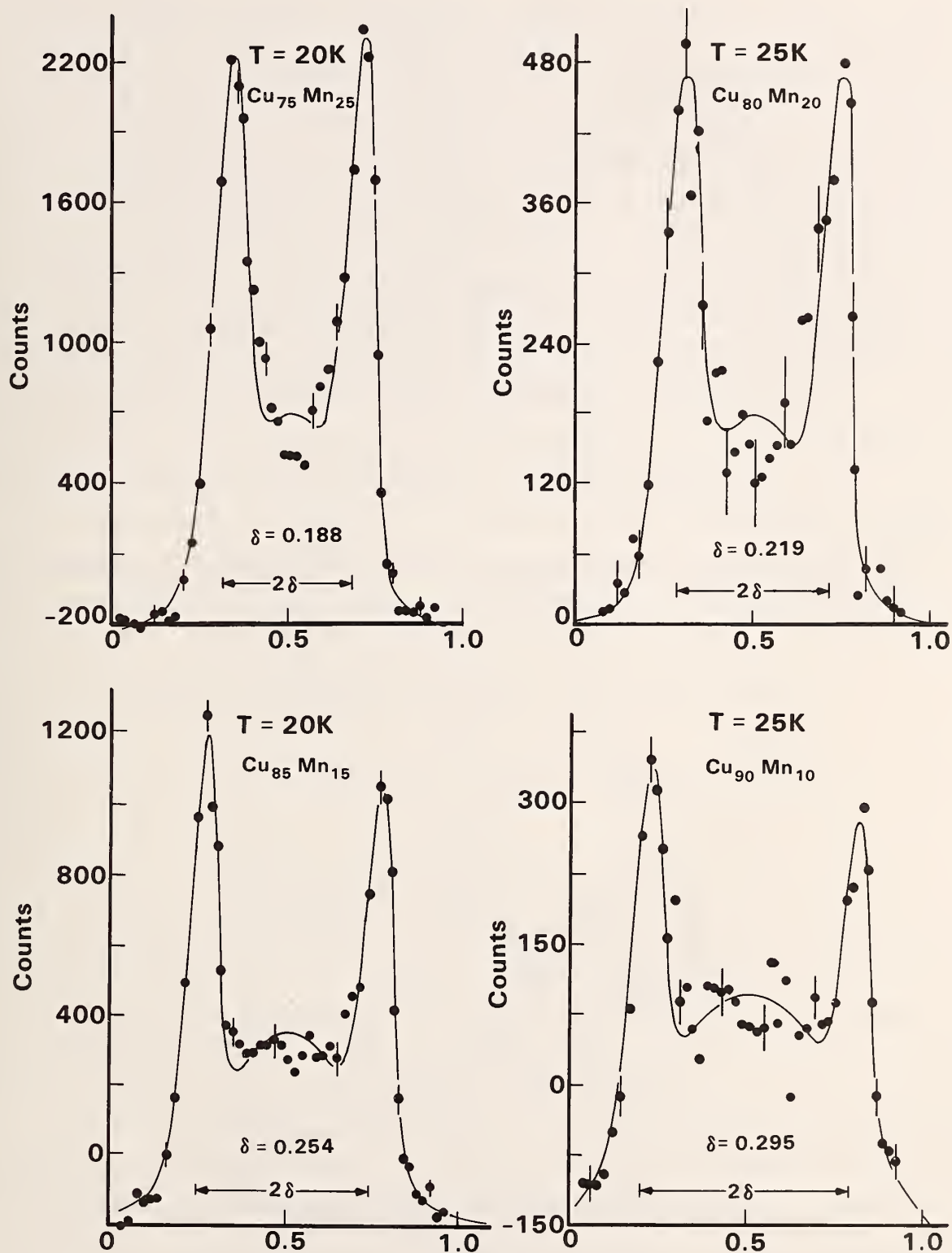


Figure 1. Scan along the line connecting the points (100) and (110). These are difference plots, i.e., the room temperature scan is subtracted from the low temperature scan leaving the magnetic component at 20-25 K.

$(1, 0.5 \pm \delta, 0)$  and equivalent positions in reciprocal space. These peaks are not as sharp as Bragg peaks, having a width corresponding to about 10 fcc unit cells, independent of Mn concentration. The magnetic scattering cross section is 3 to 5 times larger in this region of reciprocal space than near the origin of reciprocal space, and therefore must be regarded as the main source of magnetism in this system. The incommensurability parameter  $\delta$  is dependent upon Mn concentration and is 0.295, 0.254, 0.219, and 0.188 for  $x = 0.10, 0.15, 0.20$ , and  $0.25$  respectively. We have studied in considerable detail the temperature dependence of these peaks, under various spectrometer and energy resolution conditions. Example results are shown in Figure 1. These data are the results of scans along the line connecting the  $(1,0,0)$  point with the  $(1,1,0)$  point in reciprocal space. These are difference plots; that is, low temperature minus room temperature data, so that the short range atomic order peak at  $(1, 0.5, 0)$  is subtracted out. An example of the temperature dependence of the incommensurate magnetic peaks obtained in a diffraction experiment ( $E_0 = 14.8$  meV) is shown in Figure 2 for  $\text{Cu}_{.85}\text{Mn}_{.15}$ . There is no apparent anomaly at the so-called freezing temperature; in this case  $T_f \approx 70^\circ\text{K}$ . The inflection point of these

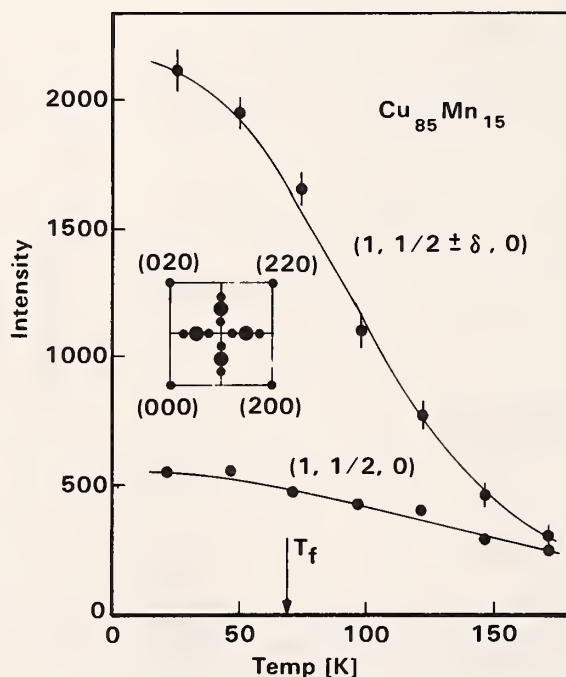


Figure 2. Temperature dependence of the intensity at  $(1, 1/2 \pm \delta, 0)$  and  $(1, 1/2, 0)$  for  $\text{Cu}_{.85}\text{Mn}_{.15}$ . This data was taken with the energy analyzer removed, and incident neutrons of energy  $E_0 = 14.69$  meV.

intensity vs. temperature curves, plotted versus Mn content is a straight line. We have carried out very high resolution experiments in which ( $E_0 = 3.6$  meV,  $\Delta E = 0.12$  meV) in an effort to isolate the elastic component of the scattering. We have found two important results in these high resolution experiments: (1) the elastic component falls off much more rapidly than that shown in Figure 2, approaching zero near 90K; and (2) the inelastic scattering component, for small energy transfers peaks near  $T_f$ . The combination of these results, along with a wide variety of additional measurements, leads us to believe that the so-called "spin glass" behavior in Cu-Mn is due to spin density waves (SDW) with a coherence length of about 10 fcc unit cells, and that the "freezing" point  $T_f$  is the Néel point representing the transition from a static "ordered" phase to a dynamic disordered phase.

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#### NEUTRON SCATTERING STUDY OF THE AMORPHOUS INVAR ALLOY $\text{Fe}_{.86}\text{B}_{.14}$

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The amorphous alloy  $\text{Fe}_{.86}\text{B}_{.14}$  has been shown to exhibit Invar characteristics<sup>1</sup> in which the thermal contraction is nearly compensated by a large positive magnetostriction. Previous studies of this system<sup>2,3</sup> show that spin waves are observable around the (0, 0, 0) point for wave vectors up to  $q = 0.12 \text{ \AA}^{-1}$ . The spin wave energies follow a normal quadratic dispersion relation and the stiffness constant,  $D$ , has a  $T^{5/2}$  dependence, in agreement with the two magnon interaction theory for a Heisenberg ferromagnet. This  $T^{5/2}$  dependence is exhibited over a very wide range of temperatures as found in other amorphous ferromagnets.<sup>4-6</sup> The stiffness constant obtained from the neutron scattering experiments is almost twice as large as calculated from magnetization measurements. This anomaly has also been reported for the crystalline Invar systems  $\text{Fe}_{.65}\text{Ni}_{.35}$  and  $\text{Fe}_3\text{Pt}$ <sup>4</sup> and is believed to be an intrinsic dynamic property of the magnetic and magneto-elastic interactions peculiar to the Invar state.<sup>2, 3</sup>



Ishikawa et al.<sup>3</sup> have reported that the intrinsic spinwave linewidths, of the  $\text{Fe}_{.86}\text{B}_{.14}$  system, vary with wave vector  $q$  as  $\Gamma = a q^2$ , showing only limited temperature dependence. This behavior has also been reported for the  $\text{Fe}_{.65}\text{Ni}_{.35}$  and  $\text{Fe}_3\text{Pt}$  Invar systems,<sup>4</sup> as opposed to the behavior of the amorphous  $(\text{Fe}_{.93}\text{Mo}_{.07})_{.8}\text{B}_{.1}\text{P}_{.1}$ <sup>5</sup> and  $(\text{Fe}_{.65}\text{Ni}_{.35})_{.75}\text{P}_{.16}\text{B}_{.06}\text{Al}_{.03}$ <sup>6</sup> non-Invar alloys, whose linewidths are consistent with the  $q^4 T^2$  relation.<sup>7</sup>

We have performed a neutron scattering experiment on a sample of amorphous  $\text{Fe}_{.86}\text{B}_{.14}$ , in order to study the spin wave dispersion relation and the intrinsic linewidths of this system. Boron enriched to 98.5 percent  $^{11}\text{B}$  was used to reduce the neutron absorption. The measurements were taken near the forward  $(0,0,0)$  beam position for wave vectors  $0.05 \text{ \AA}^{-1} \leq q \leq 0.12 \text{ \AA}^{-1}$ , at temperatures ranging from room temperature ( $0.54 T_c$ ) to 500 K ( $0.90 T_c$ ). Well-defined spin waves were observed

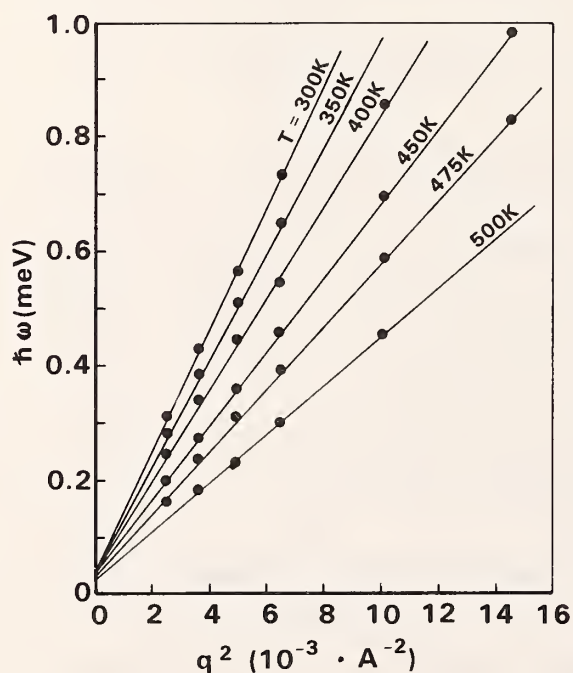


Figure 1. Spin wave dispersion relation for the  $\text{Fe}_{.86}\text{B}_{.14}$  amorphous system. The spectral weight function used was a Double Lorentzian.

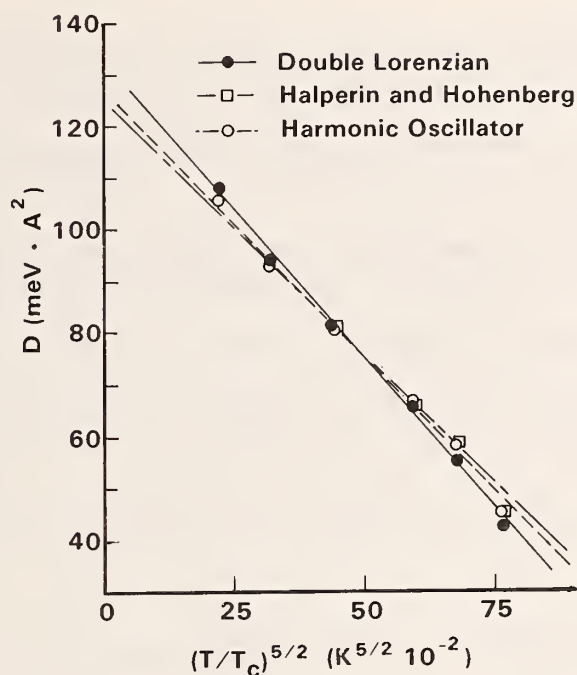


Figure 2. Temperature renormalization of the stiffness constant  $D$  with temperature as  $D = D_0[1 - c(T/T_c)^{5/2}]$ . The curves and values correspond to Double Lorentzian, Halperin and Hohenberg, and Harmonic oscillator spectral weight functions as shown.

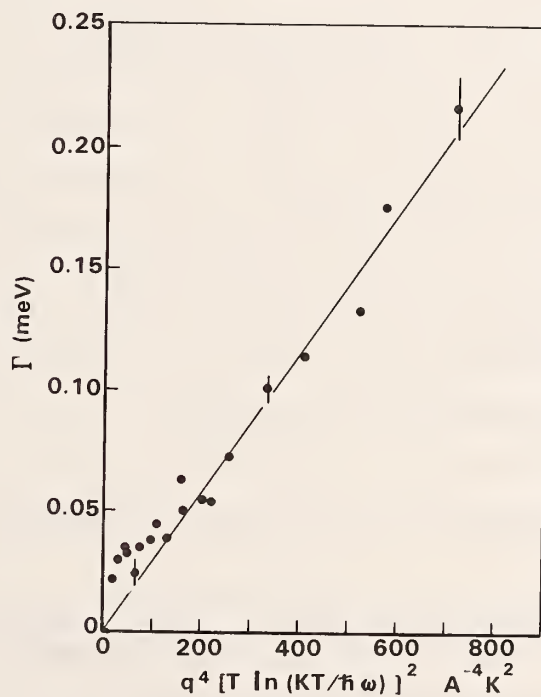


Figure 3. The intrinsic spin wave linewidths plotted versus  $q^4 [T \ln(\frac{kT}{\hbar\omega})]^2$  as predicted for the two magnon interaction theory for a Heisenberg ferromagnet.

over the whole temperature range under study. Spin wave energies and damping information were obtained from the measured profile by convolution of theoretical cross sections with the instrumental resolution. The resolution function has been calculated using the method of Cooper and Nathans.<sup>8</sup> We have used three different cross sections corresponding to Double Lorentzian, Damped Harmonic Oscillator<sup>9</sup> and Halperin and Hohenberg<sup>10</sup> spectral weight functions. The data were least-squares fitted to the convoluted cross sections to obtain values of the spin wave energies and linewidths. The three spectral weight functions all yield a dispersion relation of the form  $\hbar\omega = Dq^2 + \Delta$ ; where  $D$  is the stiffness constant;  $q$  the wave vector; and  $\Delta$  is an effective gap, due primarily to dipole-dipole interaction. Figure 1 shows the dispersion relations, calculated for the Double Lorentzian spectral weight function, for  $T = 300, 350, 400, 450$ , and  $475$  K. The gap  $\Delta \sim 0.04$  meV shows a slight temperature dependence. The stiffness constant,  $D$ , renormalizes as  $D = D_0 [1 - c(T/T_c)^{5/2}]$  in the whole range of temperatures under study (see Figure 2), where  $D_0 \sim 132$  meV  $\text{\AA}^2$  and  $c \sim 0.87$ . For this system  $D_0$  values of 138 and 118 meV  $\text{\AA}^2$  have been reported in references 2 and 3. In order to study the temperature and wave vector dependence of the spin wave intrinsic linewidths ( $\Gamma$ ) we have plotted  $\Gamma$  vs.  $q^4 [T \ln(\frac{kT}{\hbar\omega})]^2$  (see Figure 3). It is evident from this figure that the linewidth data are consistent with the form  $\Gamma \propto q^4 [T \ln(\frac{kT}{\hbar\omega})]^2$  predicted from the two magnon interaction theory of a Heisenberg ferromagnet.<sup>7</sup> The small departures (lower left part of Figure 7) correspond to temperatures lower than 400 K where the intrinsic line broadening is much smaller than the instrumental resolution (FWHM  $\sim 0.25$  meV for the region of the spin wave excitations) and the linewidths cannot be well determined.

The results in Figure 3 are in contradiction with the findings of Ishikawa et al.<sup>3</sup> who reported a dependence of the form  $\Gamma \propto T^\alpha q^2$  with  $\alpha \leq 1$ . Our result also confirms that there are no anomalies in the spin wave lifetimes which would contribute to the Invar effect seen in  $\text{Fe}_{1-x}\text{B}_x$  systems.

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# STUDIES OF THE OSCILLATORY MAGNETIC STATE IN THE SUPERCONDUCTOR $\text{HoMo}_6\text{Se}_8$

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Small-angle neutron scattering (SANS) investigations have been continued on the superconductor ( $T_c = 5.6\text{K}$ )  $\text{HoMo}_6\text{Se}_8$  to probe the nature of the oscillatory magnetic state which develops at low temperatures ( $T \sim 0.53\text{K}$ ). This sinusoidal state develops with a characteristic wave vector of  $\sim 0.09\text{\AA}^{-1}$ , corresponding to a wavelength of  $\sim 10^2$  Å. This characteristic wave vector ( $q_c$ ) then decreases as the temperature decreases, with the peak in the scattering growing in intensity.<sup>1,2</sup> The new investigations involved careful study of the time-dependence of the changes in the oscillatory state upon changing temperature and the result of applying a magnetic field (up to 0.11T) in the ordered state.

On cooling the sample to 0.286K (the lowest temperature attainable with a pumped- $\text{He}^3$  cryostat),  $q_c$  rapidly reached a value of  $0.063\text{\AA}^{-1}$ . Over a period of more than 100 hours, however, the value of  $q_c$  continued to decrease slowly, consistent with an exponential decay of the form  $q_c(t) = q_c(\infty) + a e^{-\lambda t}$ , where the asymptotic value  $q_c(\infty) = 0.0565\text{\AA}^{-1}$ , although the integrated intensity remained essentially constant. Warming the sample resulted in an initial rapid increase in  $q_c$ , followed



by a continued slow increase with time, again approaching an asymptotic limit at each temperature. In all cases, the integrated intensity remained constant during the gradual change in  $q_c$ . These long time constants for changes in  $q_c$  may result from the comparatively slow adjustment of domains in which the oscillatory wave vector lies along different directions.

Magnetic fields up to 0.11T were also applied to the sample in the ordered state. The original scattering in zero-field was isotropic about the incident beam, so that data taken on the two-dimensional SANS detector could be averaged over a complete annulus. The applied field induced asymmetries in the scattering; to study these features the data taken were averaged over smaller sections parallel and perpendicular to the direction of the applied field. Figure 1 displays such averaged data for an applied field of 0.11T at a temperature of 0.29K. It can be seen that the field induces additional scattering at very small wave vector; only the tail of the additional scattering can be observed, the remainder falling behind the detector beamstop. This small- $q$  component is induced preferentially perpendicular to the applied field, with an accompanying loss of intensity in the peak at  $q_c$ . There is no apparent shift in  $q_c$  either parallel or perpendicular to the field.

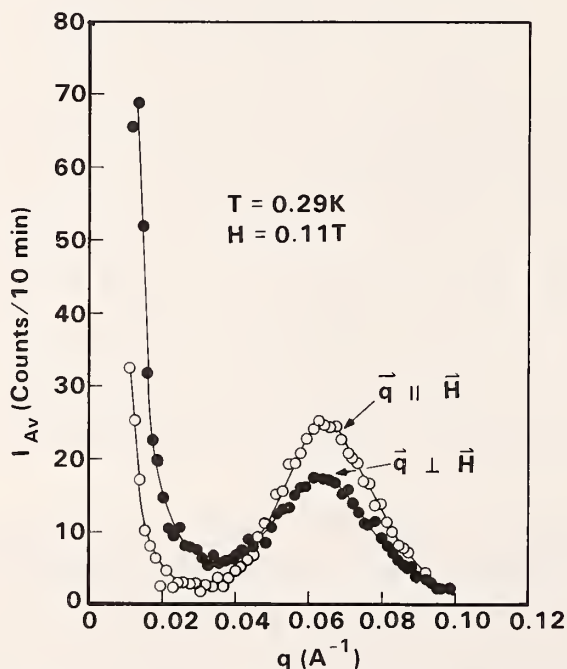


Figure 1. Average intensity versus wave vector in 0.11T applied magnetic field ( $T = 0.29K$ ), with averages calculated separately for sectors parallel and perpendicular to applied field.

Upon reducing the field to zero again, the original magnetic state is not recovered, as can be seen from Figure 2. The anisotropic scattering at small- $q$  remains, and there is a small shift in  $q_c$  perpendicular to the applied field, leading to constant-intensity contours which are prolate along the field. This post-field state persisted for times up to 45 minutes after removal of the field with little change. Upon warming the sample above the magnetic transition temperature, the scattering disappears; upon cooling, the state which occurs retains the asymmetry of the field-induced state. The source of this apparent memory of the anisotropic state in the sample is unclear at present, but may be linked to the formation of a vortex structure in the superconducting state under application of the magnetic field.

A complete understanding of the phenomena associated with this magnetic transition will require further theoretical work and a determination of the magnetic anisotropy present in  $\text{HoMo}_6\text{Se}_8$ .

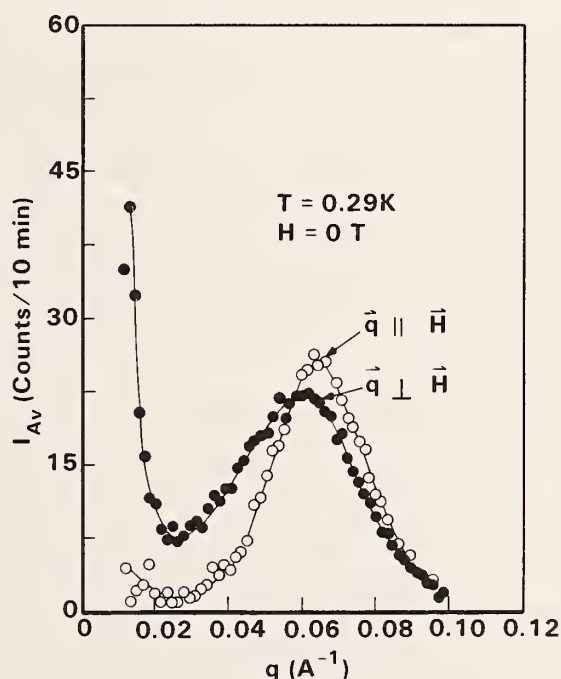


Figure 2. Average intensity (parallel and perpendicular to field) versus wave vector in 0T (0.29K) after reducing applied field from 0.11T.

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# SPIN CORRELATIONS AND DYNAMICS IN DILUTE MAGNETIC SEMICONDUCTORS

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Diluted magnetic semiconductors are alloys of ordinary semiconductors, and magnetic semiconductors. One of the most extensively studied group of those materials are manganese derivatives of the II-VI compounds, such as  $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ ,  $\text{Hg}_{1-x}\text{Mn}_x\text{Te}$ ,  $\text{Zn}_{1-x}\text{Mn}_x\text{Te}$ , and similar selenides (referred to as DMS). In these materials the metallic atoms of the host crystal lattice are randomly replaced by Mn atoms. The spin-spin exchange interactions between the localized magnetic moments of  $\text{Mn}^{++}$  ions and band electrons lead to several novel phenomena, occurring uniquely in DMS (e.g., giant Faraday rotation, or formation of bound magnetic polarons). In addition to that, the magnetic properties of DMS are interesting in their own right. Several magnetic phenomena of current interest are seen in these systems, e.g. spin-glass transitions, and magnon excitations in the spin-glass phase. From the point of view of the classification of magnetic materials DMS are diluted Heisenberg antiferromagnets. The exchange interactions between Mn ions are extremely short-range,  $J_{\text{NNN}}$  being only about one tenth of the  $J_{\text{NN}}$ . Thus, DMS are closely related to the "frustrated" (only  $J_{\text{NN}} \neq 0$ ) fcc systems, which are currently studied by various modelling techniques. Experiments on DMS are therefore of importance for theory development.

So far, neutron diffraction studies on DMS revealed that long-range magnetic order does not develop in these systems up to relatively high concentrations of Mn (up to  $x=0.7$ ). Those observation were in good agreement with the theoretical predictions by Ching and Huber<sup>1</sup>. Likewise, results of preliminary inelastic studies showed similarity to the spectrum lines calculated by these authors. Quite recently, additional theoretical results of Ching and Huber became available, namely, quantitative analysis of the ranges of spin correlations, and further results of dynamic modelling. Stimulated by this, we carried out scattering experiments on  $^{114}\text{Cd}_{0.35}\text{Mn}_{0.65}\text{Te}$ . Profiles of magnetic diffuse scattering maxima were measured at 4.2K, along various directions in q-space. Results obtained by scanning through the  $(1, \frac{1}{2}, 0)$  point in x and y direction are shown in Figure 1. The peak widths (HWHM) for x and y directions correspond to the inverse ranges of spin-spin correlations within (100) planes ( $\kappa_{\parallel}$ ), and between these planes ( $\kappa_{\perp}$ ), respectively. From data shown

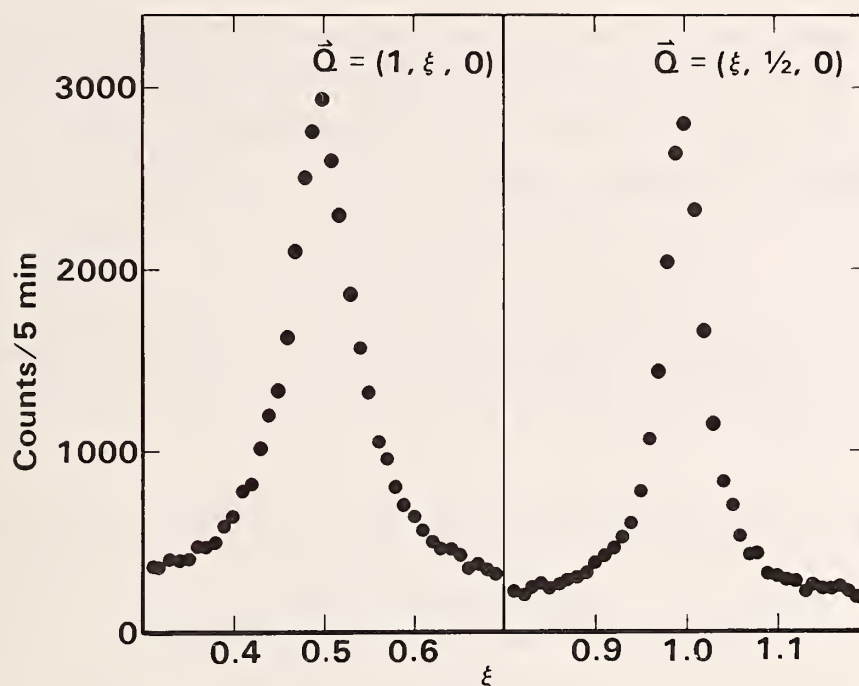


Figure 1. Scans through the  $(1, 0.5, 0)$  point of the  $q$ -space in  $[100]$  and  $[010]$  directions for  $\text{Cd}_{0.35}\text{Mn}_{0.65}\text{Te}$  single crystal at  $T = 4.2$  K.

in Figure 1 it can be estimated that the ratio  $\kappa_{||}/\kappa_{\perp} \approx 0.6$ , what is in quite good agreement with the value 0.68 obtained by Ching and Huber for a system with the same concentration of magnetic component. We measured also the inelastic magnetic neutron scattering at  $\vec{Q} = \frac{2\pi}{a}(1, \frac{1}{2}, 0)$ , and several points along  $[100]$  and  $[010]$  directions in  $q$ -space. The main features of the observed spectra, namely: the broad excitation modes, and stronger shift of the mean energy of excitations along the  $[100]$  than the  $[010]$ , are also in good agreement with model predictions. Detailed analysis of the observed data in terms of Ching and Huber theory is under way.

We carried out also preliminary powder diffraction measurements for  $\text{Zn}_{0.45}\text{Mn}_{0.55}\text{Te}$ , a new material of the DMS group which technology of growing has been recently worked out by Purdue University group. Unlike cubic DMS studied by now,  $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$  possesses the vurtzite structure. Diffusive peaks seen in the diffraction patterns at low temperatures indicate that the magnetic order is short-range, and resembles the antiferromagnetic structure of vurtzite modification of  $\text{MnS}$ .

In parallel with the experiments, Monte Carlo computer simulations of the magnetic properties of DMS were carried out. The studied model was a dilute Heisenberg antiferromagnet with nearest and next-nearest neighbor interactions, which is a classical analog of cubic DMS. In the course of this work temperature



dependences of several magnetic quantities were calculated for a system with  $x=0.70$ . The results indicate a continuous process of temperature transition, and reproduces quite satisfactorily the basic relations between results obtained by various experimental techniques on  $\text{Cd}_{0.30}\text{Mn}_{0.70}\text{Te}$ .

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### SPIN STIFFNESS ANOMALY IN THE REENTRANT SPIN GLASS $(\text{Fe}_{20}\text{Ni}_{80})_{75}\text{P}_{16}\text{B}_6\text{Al}_3$

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Low field magnetization studies have shown that the amorphous alloy  $(\text{Fe}_{25}\text{Ni}_{75})_{75}\text{P}_{16}\text{B}_6\text{Al}_3$  becomes a demagnetization-limited ferromagnet below 200K. Extrapolation to zero applied field shows that the spontaneous magnetization vanishes below a freezing temperature of 10K. Inelastic neutron scattering measurements have been performed to study the spin-wave dynamics as the spin-glass state is reentered from the ferromagnetic state. The observed magnetic excitations become critically damped below a temperature which is weakly wave-vector dependent. The peaks in the inelastic scattering at fixed  $q$  decrease in energy as the temperature is lowered towards  $T_f$  and are overdamped below  $T_f$  over the entire range of wave-vectors measured ( $0.04 \text{ \AA}^{-1} < Q < 0.18 \text{ \AA}^{-1}$ ). In the data analysis both the double Lorentzian and harmonic oscillator forms of the spectral weight function have been employed for the spectral line shapes. As shown in Figure 1, both of the spectral weight functions show a decrease in the bare spin wave frequencies ( $\omega_0$ ) as the temperature is lowered, consistent with antiferromagnetic correlations appearing in the system. The degree of softening is less when the harmonic oscillator analysis is applied to the excitations, since the harmonic oscillator prevents a description in terms of diffusive modes. In either case finite energy excitations are present in the spin

glass state, although the underdamped modes predicted by hydrodynamic theory are not observed, but may be present at smaller  $Q$ . A resolution-limited elastic component of the magnetic scattering appears below  $\sim 80\text{K}$  as  $\omega_0$  begins to decrease. As estimated from an upper limit to any possible intrinsic linewidth, this scattering is due to spins which are frozen for times at least two orders of magnitude longer than the spin wave lifetimes. In this sense, the central component represents static spatial fluctuations from the fully spin-aligned ferromagnetic state and can be interpreted as a spin-glass order parameter, although these measurements are not able to discriminate between the dynamic order parameter of Sompolinsky<sup>3</sup>, and the static

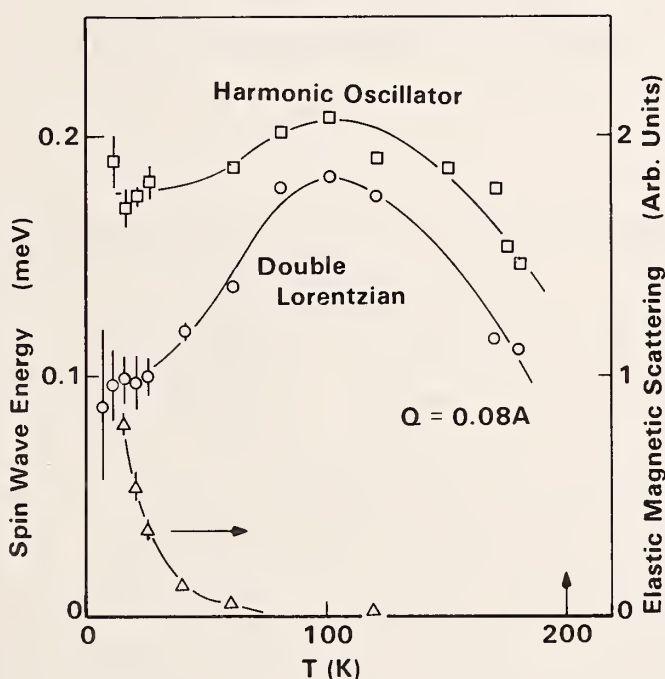


Figure 1. Spin wave energies in  $(\text{Fe}_{.25}\text{Ni}_{.75})_{.75}\text{P}_{.16}\text{B}_{.06}\text{Al}_{.03}$  at fixed  $q = 0.08 \text{ \AA}^{-1}$  as a function of temperature. Curves are shown for the energies obtained from the raw data using both harmonic oscillator and double Lorentzian forms of the spectral weight function. Both forms show a significant decrease in energy at the lower temperatures where ferromagnetism and spin glass order co-exist. The large uncertainty in the points at low  $T$  is a result of the overdamping of the spin waves. Also shown is the elastic intensity which is related to the spin glass order parameter.

order parameter of Edwards and Anderson<sup>4</sup>. In any case some type of spin-glass order coexists with ferromagnetism in the range  $10\text{K} \leq T \leq 80\text{K}$ . These results are consistent with the measurement of a finite correlation length for the magnetic fluctuations in the spin-glass state using small angle neutron scattering<sup>5</sup>.

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# MAGNETIC CORRELATIONS IN THE REENTRANT SPIN-GLASS $(\text{Fe}_{20}\text{Ni}_{80})_{75}\text{P}_{16}\text{B}_6\text{Al}_3$

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Small angle neutron scattering measurements (SANS) in the wave-vector range  $(0.01 < q < 0.10\text{\AA}^{-1})$  have been employed to determine the instantaneous two spin correlation function in the amorphous alloy  $(\text{Fe}_{20}\text{Ni}_{80})_{75}\text{P}_{16}\text{B}_6\text{Al}_3$ . Previous measurements have established that the energy transfers in this wave-vector range are sufficiently small that the SANS will directly measure the wave-vector dependent susceptibility.

The magnetic scattering above 119 K shows a conventional Lorentzian  $q$ -dependence. The temperature dependence of the width of this distribution establishes that the correlation length of magnetic fluctuations increases to an instrumental limit (400 Å) at 119 K. This agrees with low-field magnetization measurements which show that the d.c. susceptibility is demagnetization-limited in the ferromagnetic phase.<sup>1</sup>

Below  $T_c = 119\text{ K}$  the intensity of magnetic scattering first decreases with decreasing temperature as in a conventional ferromagnet and then below  $T = 80\text{ K}$  strongly increases. Energy analyzed scattering measurements for samples with higher

concentrations of Fe have shown that this increased intensity is largely due to a component which is elastic to within limits determined by instrumental resolution.<sup>2</sup> This component is identified with the spin-glass order parameter of Edwards and Anderson<sup>3</sup>,

$$q_{EA} = \langle \langle \vec{S}_i \rangle^2 \rangle,$$

where the inner brackets represent the thermal spin average and the outer brackets the configurational average. A model for the low temperature scattering function is then,

$$S(q) = A \frac{T}{\kappa^2 + q^2} + B \frac{(\kappa_D^2)^{Z-1.5}}{(\kappa_D^2 + q^2)^Z}$$

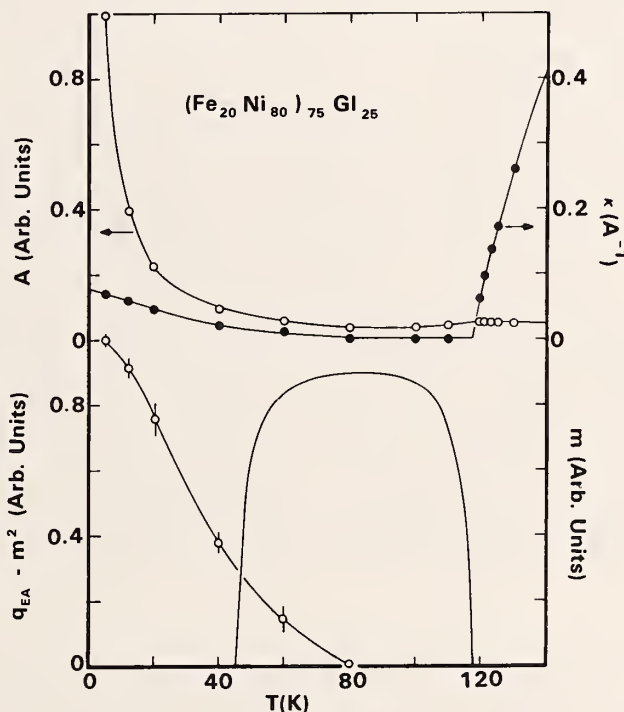


Figure 1. Temperature dependence of the inverse correlation length,  $\kappa$ , the amplitude of the wave-vector dependent susceptibility,  $A$ , and  $q_{EA} - m^2$ . In the lower half of the figure the low-field bulk magnetization is qualitatively shown. The solid curves are guides to the eye.



The first term is the Lorentzian wave-vector dependent susceptibility times the thermal population factor in the case of small inelasticity. The coefficient A would be temperature independent in an ideal ferromagnet. The second term is a generalized form describing the scattering from clusters with a distribution of sizes and shapes. For  $Z = 2$  it reduces to the Debye or random field form of a squared Lorentzian. The coefficient B is proportional to  $q_{EA} - m^2$  where  $m^2$  is the square of the spontaneous magnetization per spin ( $q_{EA} \geq m^2$  for all T).

For  $T \geq 50$  K the bulk magnetization measurements indicate that the spontaneous magnetization is non-zero, so that it is reasonable to postulate that  $\kappa = 0$  in this temperature range. In fact the fits to the data are in agreement with this conjecture. Below 50 K where the spontaneous magnetization vanishes, the best fits to the data indicate that  $\kappa$  is non-zero with  $\kappa \geq \kappa_D$ . When the parameter Z is allowed to vary the best chi-squared value is found for  $Z \sim 6$  above 50 K and for  $Z = 1.75$  below 50 K. This indicates that larger clusters are more probable above 50 K in the ferromagnetic phase than below 50 K.

The results in Figure 1 are presented for Z fixed at 2 over the entire temperature range since this does not significantly change the quality of the fits while reducing the number of free parameters. The cluster size information is then contained in  $\kappa_D$  which is zero down to 80 K. In addition  $\kappa$  is zero down to 50 K and is fixed equal to  $\kappa_D$  below this temperature. This reflects the coexistence of ferromagnetic and spin glass order between 50 K and approximately 80 K. The temperature dependence of  $q_{EA} - m^2$  is seen to be in qualitative agreement with the bulk measurements of m. The order of magnitude increase of the wave-vector dependent susceptibility and the rise in  $\kappa$  as the temperature is lowered below 80 K are both consistent with a breakup of the ferromagnetic correlations in the spin-glass phase.

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APPLIED FIELD RESPONSE OF THE SPIN GLASS STATE IN AMORPHOUS  $\text{NdFe}_2$

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The magnetic correlations and the response of the spin system to an applied field has been studied in sputtered amorphous  $\text{NdFe}_2$  using high-resolution small angle neutron scattering (SANS) techniques over the range  $0.015\text{\AA}^{-1} < Q < 0.08\text{\AA}^{-1}$ . The zero field scattering shows only a weak anomaly at the spin freezing temperature of approximately 340 K (determined from magnetization data) and exhibits strong "subcritical" scattering below  $T_f$  which increases rapidly in magnitude as the temperature is reduced. The lineshape of the scattering is Lorentzian down to the spin freezing temperature. Below  $T_f$ , the lineshape becomes increasingly non-Lorentzian and has been analyzed using a Lorentzian plus Lorentzian-squared cross-section appropriate for a random anisotropy field system. The correlation length shows a broad maximum of 170Å near 270K (which is below  $T_f$ ) and then decreases to a constant value of  $\approx 80\text{\AA}$  for  $T < 100\text{K}$ . The Lorentzian squared coefficient is negligible down to below 300K and then rises monotonically to the lowest temperatures. A similar increase is seen at low T in the Lorentzian component. The spin susceptibility defined by the coefficient of the Lorentzian term divided by the inverse correlation length squared exhibits a relatively sharp peak at 300K, close to the maximum in the correlation length.

SANS data taken in applied fields up to 18kOe at 210K and 80K produced constant intensity contours which are elliptically distorted with the  $Q \parallel H$  direction being the major axis. The overall intensity and the calculated spin correlation length both drop abruptly with increased field, the latter down to 30Å (from 175 Å at  $H = 0$ ) in a field of 4kOe at 210 K with only a small decrease at higher fields. Over the same field range, the Lorentzian squared component of the scattering is increased for  $Q \parallel H$  and decreased for  $Q \perp H$  relative to their  $H = 0$  values. This overall behavior is consistent with the field driving the dominant part of the spin system into an infinite cluster with the residual smaller spin clusters exhibiting a super-paramagnetic type response.

# SANS EVIDENCE FOR THE ABSENCE OF LONG-RANGE MAGNETIC ORDER IN AMORPHOUS $\text{Fe}_{91}\text{Zr}_9$

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Small angle neutron scattering studies of an amorphous  $\text{Fe}_{91}\text{Zr}_9$  alloy have shown that there is no transition to long-range magnetic order in contrast to results obtained from bulk magnetization<sup>1</sup> which indicated a transition to a ferromagnetic state at 220K followed by a re-entrant spin glass state near 60K. Total scattering, elastic scattering and inelastic scans were taken on a triple-axis spectrometer using a pyrolytic graphite monochromator and analyzer with 15'-12'-11'-25' effective Soller collimation. Resolution corrections for both horizontal and vertical divergences (1.5°, 2.2°, 3.8°, and 6.0°) were made.

The scattered intensity at small  $Q$  ( $0.04 \text{ \AA}^{-1} < Q < 0.2 \text{ \AA}^{-1}$ ) shown in Figure 1 shows a relatively sharp cusp at 205K followed at lower temperatures by a broad minimum. Below approximately 120K there is a further strong increase in the lowest  $Q$  intensity. The lineshape is Lorentzian in  $Q$  down to below 150K and yields a spin correlation length which reaches a maximum of only 27Å at the transition  $T_f = 205\text{K}$  and exhibits an essentially constant plateau of 23 Å down to helium temperature, with no evidence of a second transition in the 60-80K range (see Figure 2). The lineshape departs from Lorentzian below about 120K (reflecting the behavior of the lowest  $Q$  data) and can be represented by a Lorentzian (L) plus Lorentzian-squared ( $L^2$ ) cross section as follows:

$$\frac{d\sigma}{d\Omega} = \frac{A}{Q^2 + \kappa^2} + \frac{B}{(Q^2 + \kappa^2)^2}$$

where  $\kappa$  is the inverse of the spin correlation length  $\xi$  and the ratio  $A/\kappa^2$  defines the spin dependent susceptibility. This form of the cross-section is appropriate for a system in which random fields destroy the long range order and converts the delta function  $Q = 0$  scattering into the above lineshape. The ratio of the  $L^2$  to  $L$  terms increases at low  $T$  reaching 0.011 at 8K. Inelastic scattering data gave no evidence of coherent spin wave excitations at any temperature, and no significant quasi-elastic scattering.

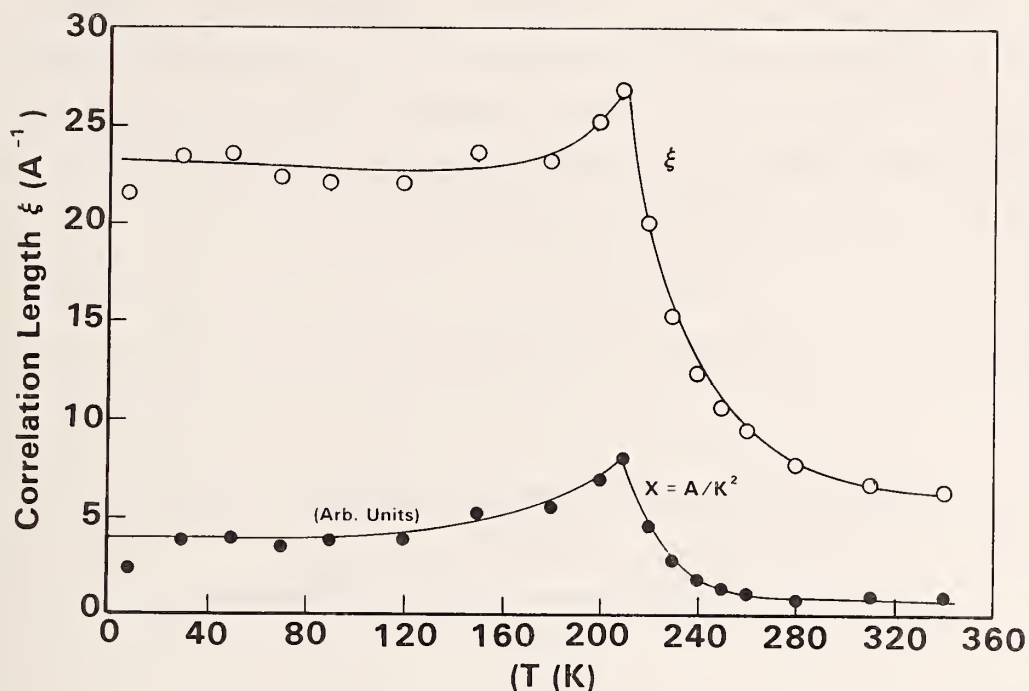


Figure 1. Temperature dependence of the total scattering at several values of  $Q$  from an amorphous  $\text{Fe}_{91}\text{Zr}_9$  alloy. The cusp near 220 K marks the spin freezing temperature. The sharp upturn in the lowest  $Q$  curves below 120K reflects the change in lineshape from Lorentzian to Lorentzian plus Lorentzian squared.

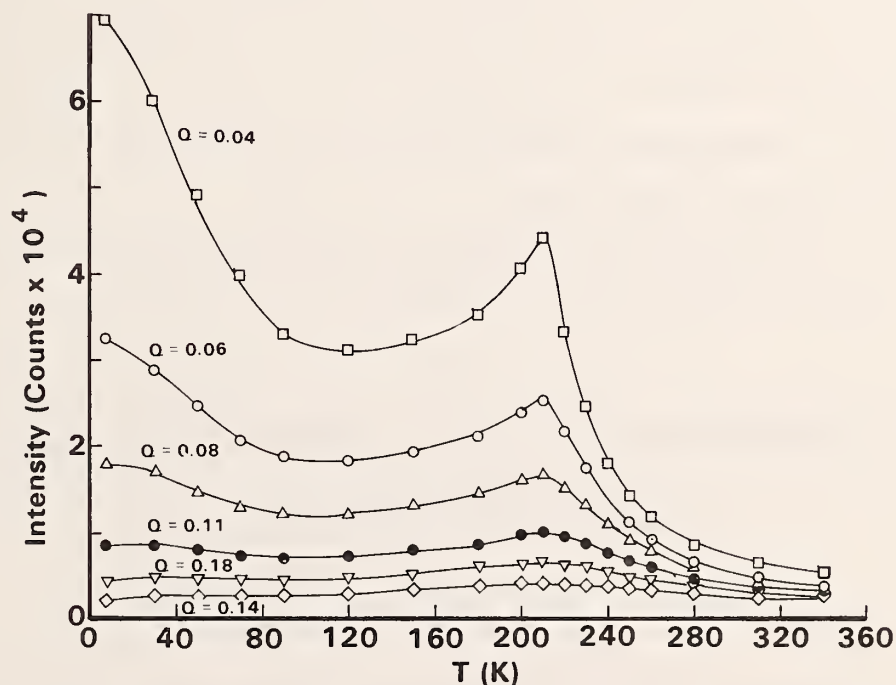


Figure 2. Temperature dependence of the spin correlation length  $\xi$  and of the wave vector dependent susceptibility  $\chi$  for amorphous  $\text{Fe}_{91}\text{Zr}_9$ .



These results confirm that  $\text{Fe}_{91}\text{Zr}_9$  enters a spin glass state below its freezing temperature of 205K with a relatively short correlation range, and no long range order. Since the concentration of Fe is far above the percolation threshold, this suggests that a very broad distribution of exchange fields arising from the random Fe site coordinates may be responsible for the spin glass state.

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### INELASTIC NEUTRON DIFFRACTION STUDIES OF ZEOLITES

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Temperature dependent inelastic neutron diffraction studies of H-rho and NaCs-rho have been initiated to study proton siting, vibrational, and mobility characteristics as the zeolite temperature approaches the in-situ temperatures commonly used in chemical catalytic processes. A pronounced change in siting is observed between room temperature and 275°C, with a shift to frequencies less than 50 meV. The constant integrated intensities at different temperatures confirm proton rearrangement rather than desorption.

Detailed studies of proton behavior over a broader temperature range and with sorbates by quasielastic and inelastic techniques are planned.

### PHONON SOFTENING IN THE MIXED LAYERED SYSTEM $\text{K}_{1-x}\text{Rb}_x\text{C}_8$

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and

J. J. Rush and N. F. Berk

Using inelastic neutron scattering, the dispersion of the longitudinal [00q] phonon modes has been measured for the first time in the mixed layered compound

$K_{1-x}Rb_xC_8$  over the whole composition range  $0 \leq x \leq 1$ . Such graphite intercalation compounds (GIC's) provide a fertile test ground for the exploration of phonons in layered mixed crystals because the phonon dispersion of the c-axis longitudinal modes is well known for the pure compounds and can be accurately described by a simple diatomic linear chain model with just two force constants. Our study shows that the mixed system, as well, is described by the same model generalized to incorporate the averaged areal mass density of the disordered alkali layers and compositionally dependent first-neighbor and second-neighbor force constants. Moreover, the second-neighbor force constant and the measured elastic constant  $C_{33}$  both show striking softening at  $x = 0.65$ . Our work has led us to suggest that this softening, and possibly other anomalies at this composition that have been recently reported, is caused by an asymmetric composition-dependent charge transfer between the mixed alkali layers and the graphite layers. It is also interesting to note that the study did not reveal any neutron scattering that could be attributed to defect vibrational modes in the bands or in the gap.

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### THEORY OF ALKALI CYANIDES

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and

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In the past year, significant progress has been made in the theory of translation-rotation coupling in alkali cyanides. In particular, a new mode-coupling approach shows promise for the explanation of the damping of optic phonons in the cyanides--a fact well established experimentally (and in molecular dynamics simulations) but not heretofore unexplained by theory. In addition, new calculations of self-energies and other local properties are pointing towards modification of earlier theoretical results for transition temperatures and neutron cross-sections.

STRUCTURE OF ALKALI CYANIDE-ALKALI HALIDE CRYSTALS

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We have extended our earlier measurements of the structure of  $(\text{KCN})_x(\text{KBr})_{1-x}$  by neutron powder diffraction to  $(\text{KCN})_x(\text{KCl})_{1-x}$ . In contrast to the KBr mixtures, which first go to a monoclinic structure at low temperatures, KCl mixtures go directly to an orthorhombic structure similar to that of pure KCN. This is true even at a value  $x = 0.80$ , which is the lowest value of  $x$  at which a transition occurs. The KBr samples for  $x = 0.6$ , the lowest  $x$  for which a transition occurs, go monoclinic and remain monoclinic down to the lowest temperatures). This contrast in behavior must be related to the different size of the  $\text{Br}^-$  and  $\text{Cl}^-$  ions, but the origin of the effect is as yet unknown. This new structural information helps to explain the earlier observation that  $\left(\frac{2T_c}{2x}\right)$  is quite different for the two systems. When one compares  $\left(\frac{2T_c}{2x}\right)$  for transition to the orthorhombic phase, the two systems are much more similar. Since the monoclinic phase observed in the Br mixtures is closely related to the metastable monoclinic phase observed in KCN subjected to repeated stresses, a possible explanation for all observations is that the range of existence of the orthorhombic phase is the same in both systems, and that the monoclinic phase is not stable against strains (such as the lattice mismatch caused by the  $\text{Cl}^-$  ions).

NONDESTRUCTIVE CHARACTERIZATION OF SUBSURFACE RESIDUAL STRESS IN DEPLETED URANIUM

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Depleted uranium -0.75 wt% Ti alloy ("DU") has become a principal material for armor-piercing projectiles because of its high density, hardness, ductility, and high ultimate tensile and yield strengths. These properties are achieved by a fabrication process which involves a fast quench to ambient temperature from the  $\gamma$ -phase ( $\sim 800^\circ\text{C}$ ), followed by aging at  $\sim 400^\circ\text{C}$ . This yields the desired mechanical properties with the Ti "dissolved" in the single-phase  $\alpha'$ -U host lattice. However, optimization of performance has probably not been achieved because of an inability to characterize certain properties in the course of the fabrication process. One of the most important of these is residual stress.

Table I. x-ray/Neutron Comparison

| Element (Atomic Number) | $t_{1/2}$ (1.54 Å X-rays) | $t_{1/2}$ (1.80 Å Neutrons) |
|-------------------------|---------------------------|-----------------------------|
| Al (13)                 | 0.0530 mm                 | 71.0 mm                     |
| Ti (22)                 | 0.0076                    | 15.9                        |
| Fe (26)                 | 0.0027                    | 6.1                         |
| W (74)                  | 0.0021                    | 6.5                         |
| U <sup>238</sup> (92)   | 0.0015                    | 13.6                        |

Table 2. U<sup>238</sup>-0.75 wt% Ti Samples

| Property/Treatment                       | DU1 | DU2 |
|------------------------------------------|-----|-----|
| Extrusion (10X Reduction in Area)        | X   | X   |
| Solutionizing (2 hrs., 850°C, vacuum)    | X   | X   |
| Furnace Cooled                           | X   |     |
| Quench                                   |     | X   |
| Rotary Straightened                      |     | X   |
| Aged                                     |     | X   |
| $\alpha$ -U + TiU <sub>2</sub> Structure | X   |     |
| $\alpha'$ -U Structure                   |     | X   |

x-ray diffraction for residual stress analysis (XRDRSA) has been developed so successfully that it is now a routine method for nondestructive determination of surface stresses in metals. In fact, in the last few years portable devices for field use have become commercially available. However when applied to DU, grain size, surface oxidation, and other effects have produced very serious problems for XRDRSA.<sup>1</sup> Alternative nondestructive techniques - such as ultrasonics, eddy current, etc. - have seen only limited success on other metals and have not proven useful for DU. Until now, the technique which has been used with the greatest degree of success is the (destructive) Sach's boring-out method.<sup>1</sup> Applied to DU, it is slow, expensive, requires special surface coating, special boring equipment, and the use of strain gauges. In addition, certain assumptions are required to extract stress values for the cylindrical specimens. For example, hoop and axial stresses are assumed to vary only with radial distance from the cylinder axis. The fact that the DU bars are bowed when removed from the quench bath shows this to be incorrect.

Recently, we have demonstrated that energy-dispersive neutron diffraction (EDND) is a viable technique for the measurement of subsurface residual stress in highly textured metallurgical samples.<sup>2</sup> As shown by the attenuation thicknesses for half-intensity loss,  $t_{1/2}$  listed in Table 1, DU is a very favorable material for neutron diffraction examination. In contrast, a 1.54 Å x-ray beam is attenuated by one-half in 1.5  $\mu$ m of DU, which is less than the typical grain size of 5-10  $\mu$ m.

We have applied EDND to the determination of subsurface residual stresses in two samples of DU which differed in thermo-mechanical history as shown in Table 2.



It was expected that DU1, the furnace-cooled specimen, would exhibit near-zero residual stresses, while the stresses in DU2 would be large with steep gradients.

The measurement geometry is shown in Figure 1. The indicated differential volumes are defined by apertures in cadmium masks mounted on the incoming- and scattered-beam collimators.<sup>2</sup> Strains were determined for the (111) reflection at a scattering angle of  $72.4^\circ$  with an instrumental resolution  $\Delta d/d \sim 0.007$ . The unstressed d-spacings,  $d_0$  (111), for both  $\alpha$ -u and  $\alpha'$ -u were determined by high-resolution neutron powder diffraction and total-profile analysis using 1 cm. diameter x 1 cm. long samples and sample spinning (to minimize texture effects).

Neglecting shear stresses, measured strain is related to residual stress by

$$E_{\phi\chi} = 1/2S_2(hkl)[\sigma_{rr} \cos^2\phi \sin^2\chi + \sigma_{\theta\theta} \sin^2\phi \sin^2\chi + \sigma_{zz} \cos^2\chi] + S_1(hkl)[\sigma_{rr} + \sigma_{\theta\theta} + \sigma_{zz}],$$

where  $z$  corresponds to the cylinder axis,  $\chi$  is the angle measured from the  $z$  axis, and  $\phi$  is measured relative to the  $r$ -direction.

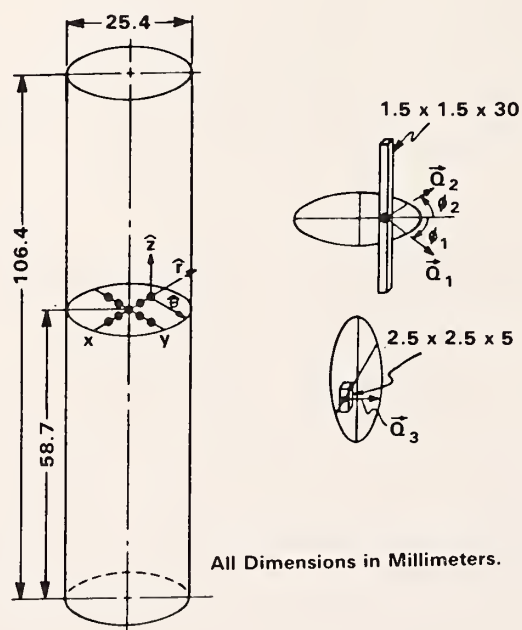


Figure 1. Overall geometry of the DU samples and points at which measurements were made. Also shown are the differential volume examined for  $\vec{Q}$ s in the  $r$ - $\theta$  plane (upper right) and parallel to the cylinder axis ( $\vec{Q}_3$ ). The  $Q$ -direction corresponds to the bisector of the angle between incident and diffracted beams.

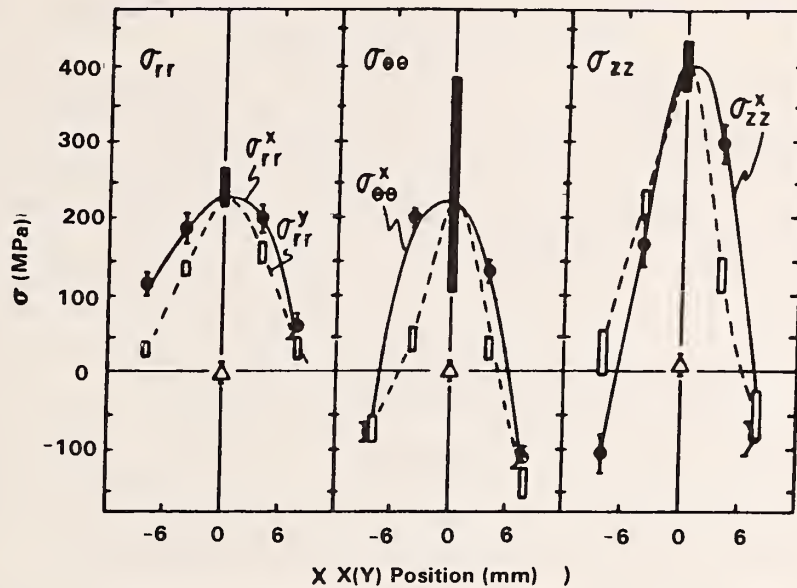


Figure 2. Residual stresses in the two depleted uranium samples [DU1 results are shown as triangles at  $x(y) = 0$ ]. The procedure employed is described in the text.

In this case the anisotropic diffraction constants  $S_i$  are approximated as

$$1/2 S_2(hkl) = (1+\mu)/E \text{ and } S_1(hkl) = -\mu/E$$

where  $E$  is Young's modulus and  $\mu$  is Poisson's ratio, with  $E = 165480$  MPa and  $\mu = 0.21$  in this case. The residual stresses obtained for DU1 and DU2 are shown in Figure 2. Because strains measured for several points in DU1 were constant within the standard deviations of the least-squares fit  $d$ -spacings, only the axial point is shown.

The measured stress distributions confirm the applicability of the EDND technique to DU. Overall, the stress distribution obtained for DU2 is in good agreement with what would be expected for a rapidly-quenched cylinder and with Sach's boring-out results.<sup>1</sup> However, clear asymmetries in stress distributions are present as indicated by the fact that measured stresses along the two orthogonal diameters ("X" and "Y") do not coincide (i.e.,  $\sigma_{rr}^X \neq \sigma_{rr}^Y$  etc.) These asymmetries may arise from the rotary straightening of DU2; however, the rods are, in general, found to be bent when removed from the quench bath. This suggests that either quenching is non-uniform (possible because many rods are "bundled") or texture in the uranium introduces anisotropy in the stress distribution.

These results represent the first nondestructive determination of subsurface residual stresses in DU by any technique. For the future this provides the prospect of examining stress distributions--for DU and other materials--for a single piece in each stage of the fabrication process.

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### STUDY OF MATERIALS SUBJECT TO IMPACT

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High resolution neutron diffraction measurements have been used to characterize specimens used for fracture dynamic studies. Two samples of a Zirconium alloy (cubes, 11 mm on a side) were measured: one as-received and the other after impact by a 16 mm aluminum plate at 0.9 km/sec. Seventeen distinct reflections were observed for each sample in the range 32-107 degrees at the neutron wavelength of 1.54 Å. Least square Gaussian fits to the profile of each peak yielded a full-width-at-half-maximum (FWHM) for each reflection. Although the peaks for the as-received sample were only slightly broadened as compared to an  $\text{Al}_2\text{O}_3$  powder sample standard, the peaks of the impacted sample were considerably broadened. For example, the (114) reflection at  $2\theta = 100.7^\circ$  had a FWHM =  $0.515^\circ$  for the as-received sample but a FWHM =  $0.715^\circ$  for the impacted sample. The principal causes of peak broadening are a decrease in the size of the coherent diffracting regions (particle size broadening) and internal strains. These two parameters were determined by fitting the data to calculated expressions for the FWHM as a function of scattering angle with the result that the strain was determined to be  $\sim 1.6 \times 10^{-3}$  while the "particle size" was in the range 1000 to 3500 Å depending on the exact form of the distribution of strains and particle sizes (Gaussian or Cauchy).<sup>1</sup> Of the two effects internal strains are the main cause of the broadening. The magnitude of the resultant internal stress due to these strains is of the order of the yield stress in this material. Although the cube remained intact after impact, subsequent sectioning revealed many internal cracks.

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# SPHERICAL-MODEL ESTIMATE OF THE UPPER BOUND FOR THE ABSORPTION OF CAPTURE-GAMMAS IN THE NEUTRON COLD SOURCE

R. S. Carter and R. C. Casella

We have considered an idealized model of the cold source which allows analytic solutions for the absorption of those gamma rays which are produced by neutron capture in the cold source. The model consists of a sphere of deuterated ice of radius  $a$  and gamma absorption coefficient  $\mu_1$ , surrounded by a contiguous aluminum shell of uniform thickness  $t$  and absorption coefficient  $\mu$ , where  $t \ll a$ . Gammas are assumed produced in the shell at a rate  $s(\theta, \phi) = \rho(\theta, \phi)t$  per unit area per unit time. Neutron capture within the ice is neglected. The model allows one to calculate the fraction of the total gamma production rate  $a^2 \int d\Omega s(\theta, \phi)$  which is absorbed in (a) the ice and (b) the aluminum shell in a simple way and can serve as a basis for more elaborate analyses. Since the surface-to-volume ratio is minimal for a sphere, one expects a smaller fraction of the gammas will escape than would be the case from a non-spherical configuration of equal volume. Thus the model should yield an estimate of the upper bound to the actual rate of absorption of the capture-gammas for a fixed volume of ice and a given rate of neutron capture in the surrounding shell. The treatment presented here deals with only one facet of the overall analysis of the cold source. Even then, further corrections for the realistic configuration are required and have been estimated. Nonetheless, the relatively simple approach discussed contains the essence of this one aspect of the analysis.

Once produced via neutron capture in the outer shell, gammas are absorbed in three stages: (i) primary local absorption by the shell immediately after their production therein, (ii) absorption of the inwardly directed gammas by the ice sphere during their traversal thereof, and (iii) secondary absorption in the surrounding shell of gammas which have negotiated the sphere but must traverse the aluminum shell from within to escape to the outside. In the limit as the thickness  $t \rightarrow 0$  such that both  $\mu$  and  $s(\theta, \phi)$  remain finite, only the ice absorbs the inwardly directed source current  $j_s(\theta, \phi) = (1/2) s(\theta, \phi)$ . Of this, a fraction  $f_{esc}^{in}$  escapes after having traversed some part of the sphere, where

$$f_{esc}^{in} = (1/2\mu_1 a)(1 - e^{-2\mu_1 a}). \quad (1)$$

The fraction of the total rate of gammas produced which escapes is equal to  $1/2 + 1/2 f_{esc}^{in}$ , whence the fraction absorbed is given by



$$f_{abs}^0 = (1/2)(1 - f_{esc}^{in}). \quad (2)$$

The above results hold for gammas produced at each point  $(\theta, \phi)$  on the surface. They are exact in the limit as  $t \rightarrow 0$  with  $\mu$  remaining finite. Moreover, they are independent of the angular distribution of the source strength  $s(\theta, \phi)$ .

To incorporate finite-thickness corrections when  $\mu t \ll 1$ , we employ the infinite-plate approximation at each position  $(\theta, \phi)$  on the shell. This approximation is valid when both  $(t/a)$  and  $(1/\mu a)$  are small compared with unity. Then

$$j_s(\theta, \phi) = (\rho t/2) (1/\mu t) [1/2 - E_3(\mu t)], \quad (3)$$

where  $E_n(x)$  is the tabulated exponential function:

$$E_n(x) = \int dy (1/y^n) e^{-xy}. \quad (4)$$

The fraction locally absorbed  $f_{abs}^{loc}$  equals  $1 - 2j_s/\rho t$ .

Next finite- $t$  corrections are considered for the fraction  $f_{abs}^{ice}$  of gammas absorbed in the ice (process ii). The fraction  $f_{esc}^{in}$  of inwardly moving impinging gammas which escapes the ice is independent of  $t$  and is given by eq. (1). the fraction of these inward movers which is absorbed in the ice equals  $1 - f_{esc}^{in}$ , whence,

$$f_{abs}^{ice} = (j_s/\rho t)(1 - f_{esc}^{in}). \quad (5)$$

Finally, we have estimated the amount of secondary absorption of the gammas in the shell (process iii). In terms of the spherical average

$$\langle j_s \rangle = (1/4\pi) \int d\Omega' j_s(\theta', \phi'), \quad (6)$$

we find the approximate result

$$f_{abs}^{sec} = (\langle j_s \rangle / \langle \rho t \rangle) f_{esc}^{in}(\mu_1 a) [1 - E_2(\mu t)]. \quad (7)$$

Here  $f_{esc}^{in}(\mu_1 a)$  is given by eq. (1) and  $\langle j_s \rangle / \langle \rho t \rangle = j_s/\rho t$ , as given by eq. (3). In the limit as  $t \rightarrow 0$ ,  $j_s/(\rho t) \rightarrow 1/2$  and  $E_2(\mu t) \rightarrow 1$ , whence  $f_{abs}^{loc} \rightarrow 0$ ,  $f_{abs}^{sec} \rightarrow 0$ , while  $f_{abs}^{ice} \rightarrow f_{abs}^0$ , the latter given by eq. (2). That is, the earlier result for zero shell thickness is recovered. For finite  $t/a$ , finite curvature corrections to the infinite-plate approximation in treating the shell also enter.

COLD NEUTRON SOURCE -  $D_2O$ 

R. S. Carter

During the past year, additional funds became available to expedite the installation of the  $D_2O$  ice cold source.

The radiation shielding around the cold source cryostat is a separate unit mounted on a separate plug (see Figure 1). The shielding material is primarily bismuth, and the unit is referred to as the bismuth tip. This unit is completed and ready for installation. The safety analysis has been completed, reviewed, and approved by the NBSR Safety Evaluation Committee. It will be installed when the cold source cryostat is installed.

The original cold source cryostat was made of aluminum and included a beryllium filter placed in the reentrant hole in the ice. The cryostat was redesigned to provide complete helium containment of the insulating vacuum and to omit the beryllium filter. Magnesium alloy was selected as the material of fabrication in order to decrease heat generation from capture gamma rays. The low neutron capture cross section of magnesium reduced the heat generation by a factor of three. The new design has been completed and put out for bids.

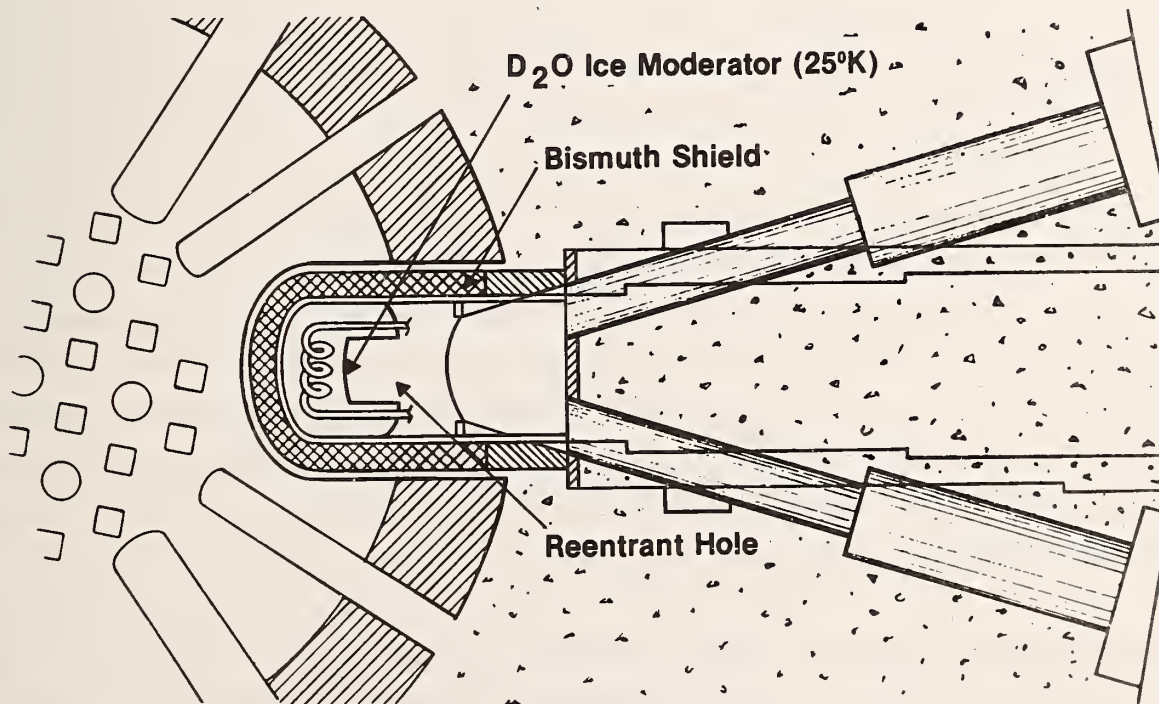


Figure 1. Cold neutron source.

# SEARCH FOR CHARGE DENSITY WAVES AND OTHER EXPERIMENTS ON POTASSIUM

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The most straightforward method of studying charge density waves is by diffraction experiments. CDWs lead to incommensurate modulation of the normal crystalline periodicity, giving rise to satellites of Bragg reflections seen in X-ray and neutron diffraction patterns. So far, such satellites have been observed in layered and one-dimensional compounds<sup>1</sup>, and in many metals, e.g.  $\alpha$ -Uranium. There is much evidence, however, that CDWs exist also in alkali metals; reviews of these results are given in articles of Overhauser and co-workers<sup>2</sup>. The feasibility of diffraction studies on potassium is also discussed in these papers. As follows from elementary considerations, the position of a satellite peak in Q-space is given by  $\vec{G} + \vec{Q}$ , where  $\vec{G}$  is the (110)-reciprocal lattice vector ( $|\vec{G}| = 1.414 \frac{2\pi}{a}$ ), and  $\vec{Q}$  is the wave-vector associated with CDW. Optical data indicate that  $\vec{Q}$  in potassium is nearly parallel to one of the [110] axes, and its length is  $\sim 1.38 \frac{2\pi}{a}$ . These numbers determine approximately the satellite positions (as domains with different  $\vec{Q}$ s may form in the crystal, satellites with various intensities should occur at 48 symmetry related positions surrounding each bcc Bragg reflection). Unfortunately, the estimated satellite intensity is only  $\sim 10^{-5}$  of the intensity of the underlying bcc Bragg reflections. This fact, combined with the small distance from the (110) Bragg peak, clearly points out the scale of difficulty of an experiment. However, diffraction data is crucial for the theory of CDWs in alkali metals: first, as a qualitative confirmation; secondly, for accurate determination of the  $\vec{Q}$  vector, important for quantitative analysis.

In view of this, we carried out neutron diffraction experiments on potassium. The sample was a cylindrical single crystal (1'' in diameter, and 3'' in height), with the  $[01\bar{1}]$  axis vertical. A triple axis spectrometer was used, with a pyrolytic graphite (PG) monochromator and analyzer, and a PG filter. Several precautions were taken in order to avoid spurious peaks. One class of such effects is multiple



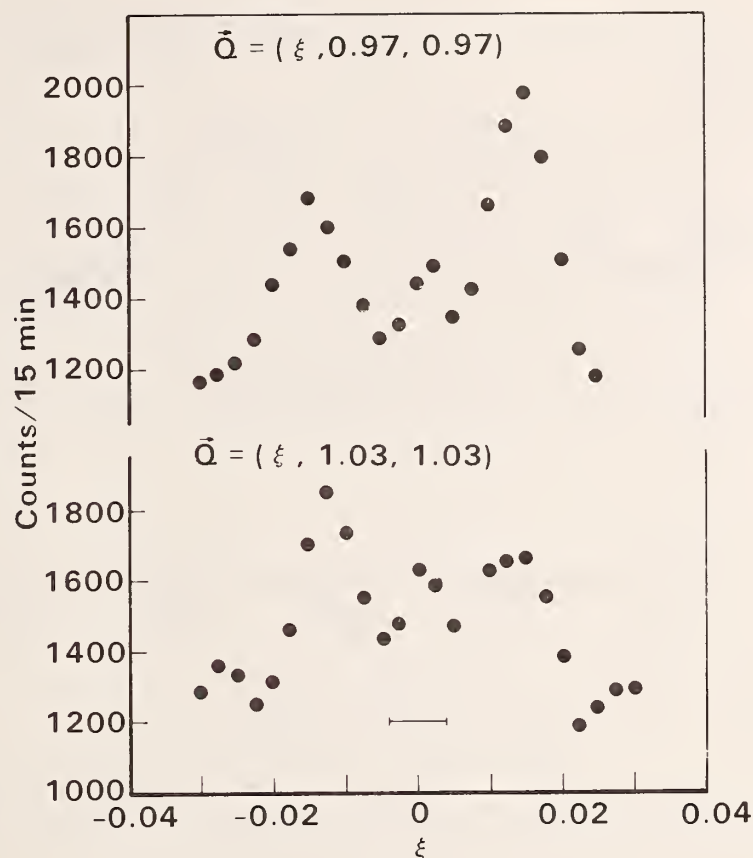


Figure 1. Peaks seen in the vicinity of the (011) Bragg reflection in potassium. Small peaks in the center ( $\xi \approx 0$ ) are remnants of the Bragg peak. The vertical bar is the width (FWHM) of the Gaussian instrumental resolution function.

scattering. As multiple reflections vary strongly with wavelength, two different  $\lambda$ s were used. Another source of artifacts, thermal diffuse scattering (TDS), was taken into consideration with special concern. TDS was reduced by maintaining a low sample temperature (4.2K), and performing an energy analysis of the scattered beam. Such precautions might still be insufficient. Therefore, calculations of TDS were carried out. A computer program was employed<sup>3</sup>, calculating the inelastic spectrum for a given scan direction, taking into account all essential crystal and instrumental data. Computed results were "calibrated" by comparing calculated and measured phonon peaks.

We carried out scans in various direction in Q-space in the neighborhood of the (011) and (200) reflections. Several peaks were seen in diffraction patterns; however, most of them could not be reproducibly observed. The only fully reproducible effect were four peaks occurring in the scanning directions  $\vec{q} = (\xi, 0.97, 0.97)$ , and  $(\xi, 1.03, 1.03)$  for  $\xi = \pm 0.015$  (Fig. 1). The widths of these peaks



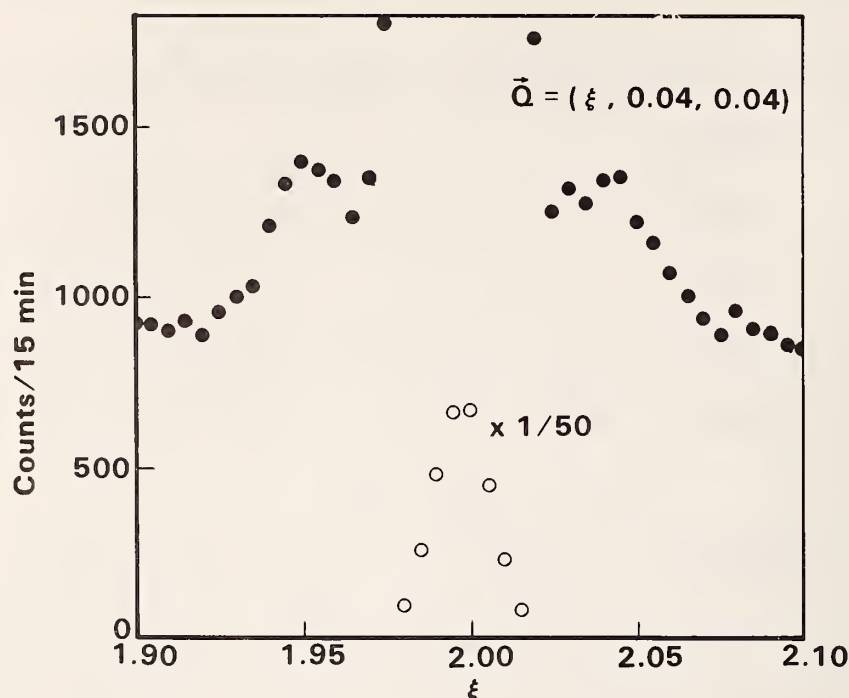


Figure 2. As in Figure 1, for the (200) reflection.

are in agreement with the corresponding instrumental resolution. Because of the limited resolution in the longitudinal direction, we were not able to resolve the peaks accurately enough from the (011) peak. Therefore, we still cannot exclude that the effect observed is associated with a certain kind of "ridge" descending from the main reflection. If assuming, however, that the peaks observed are CDW satellites, one can estimate on that basis where other satellites should be seen. In the vicinity of the (011) reflection these predicted peaks have either zero intensity, or interfere with the extended shoulders of the Bragg peak produced by a small fraction of mosaic blocks deviated far from the mean orientation. More favorable conditions are offered by the (200) reflection. Peak-like effects were reproducibly observed, indeed, for scanning direction  $\vec{Q} = (2+\xi, 0.04, 0.04)$  at  $\xi \approx \pm 0.045$  (Fig. 2); this is close to one of the predicted points. As before, the spectrometer resolution was insufficient for obtaining convincing results for the perpendicular scan direction. Scans performed at other expected regions of satellite occurrence gave negative results. However, the estimated positions may be somewhat ambiguous, when based only on two components of  $\vec{Q}$  that can be evaluated from the peaks near the (011) reflection. In fact, satellites may be located beyond the experimental plane and missed because of too tight a vertical collimation.

So far, we have not collected enough evidence for drawing final conclusions. More experiments are necessary; the data already existing provide indications for further experimentation.

We also performed measurements of phonon dispersion relations in potassium. This experiment is related to studies of the local field corrections to the dielectric function. Investigation of the effects of the singularity in local field corrections at  $q=2k_f$  on the phonon spectrum by Wang and Overhauser<sup>4</sup> shows that the singularity will influence the phonon dispersion relations along certain trajectories in q-space. As experimental data for potassium are available only for high-symmetry directions, such studies require new research. We measured the inelastic phonon spectra for trajectory  $\frac{2\pi}{a}(0.36, 0.36, 2+\xi)$ , and several other lines in q-space parallel to this direction. Experiments for other trajectories are also planned.

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1. J. A. Wilson, F. J. DiSalvo, and S. Mahajan, Adv. Phys. 24, 117 (1975)
  2. A. W. Overhauser, Advances in Physics 27, 343-363 (1978); G. F. Giuliani and A. W. Overhauser, Phys. Rev. B 23, 3737-3743 (1981), and references therein
  3. Unpublished; the program was originally created by R. Pynn and S. A. Werner (1971); running versions are kept at NBS, and BNL.
  4. Y. R. Wang, M. Ashraf, and A. W. Overhauser (1983), unpublished.

RECENT ADVANCES IN NEUTRON OPTICS

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A range of phenomena similar or analogous to those of classical optics is exhibited by slow neutrons. During the past decade considerable interest has been generated in this field from the point of view of fundamental physics. This has been due largely to the successful application of the perfect silicon crystal interferometer to neutron experiments, and to the increased availability of more intense sources of long wavelength neutrons. Neutron optical ideas and techniques play an important role in all aspects of neutron scattering technology, in particular in the extraction, filtering and monochromation of beams. This work represents the most recent, comprehensive review of this important field of neutron science. It will be published in the book Neutron Scattering, (Chapter 4), edited by D. L. Price and K. Sköld, Academic Press (1984). It is 78 pages in length, with 166 references and 39 figures. It contains the following main sections:

1. The optical analogy and the refractive index.
2. Refraction and reflection.
3. Diffraction by macroscopic objects.
4. Interference and interferometry.
5. Applications of neutron interferometry in fundamental physics.
  - Gravity and inertia
  - Verification of quantum mechanical principles
  - Tests of non-standard quantum mechanics
6. Neutron optics in perfect crystals.
7. Conclusion and future prospects.

NONLINEARITY IN WEAK MAGNETIC FIELDS INDUCED BY NEUTRON-ANTINEUTRON OSCILLATIONS  
 IN NEUTRON INTERFEROMETRY AND SPIN RESONANCE

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The breaking of exact baryon-number conservation in unified theories of the fundamental gauge interactions, has led to extensive searches for proton decay and neutron-antineutron ( $n\bar{n}$ ) oscillations, thus far without confirmed experimental evidence for either process. In some theories,  $n\bar{n}$  oscillations can occur even in the absence of proton decay. For unbound neutrons, the present experimental limit on the relevant parameter  $\delta < 7 \times 10^{-22}$  eV, is obtained by looking for annihilation in a downstream target of an  $\bar{n}$  generated with probability  $P_{\bar{n}}(t)$  from an initial reactor-produced neutron after a flight time  $t$ .<sup>1</sup> A more stringent, but less direct, limit on  $\delta$  exists from stability in oxygen nuclei. I have examined the possibility of detecting unbound  $n\bar{n}$  oscillations, not by observing the  $\bar{n}$  directly, but rather by employing some very sensitive technique, such as neutron interferometry or spin resonance,<sup>2</sup> to detect a nonlinear variation with magnetic field  $B$ , which is associated with a minute shift of the neutron energy induced by the exchange of heavy  $X$  quanta endemic to unification theories.

Assuming CPT as well as CP invariance and neglecting decay, the phenomenological Hamiltonian in the particle rest frame can be written in the form  $H = m - \vec{\mu} \cdot \vec{B} + \delta \lambda_x$ , where  $\vec{\mu} = \lambda_z g \mu_N \vec{\sigma}$  is the  $n$  (or  $\bar{n}$ ) magnetic moment expressed in terms of the nuclear magneton  $\mu_N$ , neutron  $g$ -factor, and Pauli spin matrices  $\vec{\sigma}$ . ( $\lambda_x$  and  $\lambda_z$  are the analogues of isospin matrices in the  $|n\rangle$ ,  $|\bar{n}\rangle$  basis, where, e.g.,  $\lambda_x |n, \sigma_z\rangle = |\bar{n}, \sigma_z\rangle$ .) As is well known, the eigenvalues of  $H$  are  $M_{\pm}(\beta) = m \pm (\beta^2 + \delta^2)^{1/2}$ , each doubly degenerate in ordinary spin ( $\uparrow, \downarrow$ ).  $\beta/B = |g\mu_N| \sim 6.0 \times 10^{-12}$  eV/gauss. If, say,  $|\psi(t=0)\rangle = |n\uparrow\rangle$ , then one obtains the known result, which for  $(\delta/\beta)^2 \ll 1$  is

$$P_{\bar{n}\uparrow}(t) = |\langle \bar{n}\uparrow | \psi(t) \rangle|^2 = (\delta/\beta)^2 \sin^2 \beta t. \quad (1)$$

(For the moderately reduced fields and typical flight times employed in the current nonstorage configuration,  $\beta t \ll 1$  and  $P_{\bar{n}}(t) \approx \delta^2 t^2$ .) I have examined the other connected amplitude which, for the same initial condition, reads

$$\langle n\uparrow | \psi(t) \rangle = e^{-imt - i\beta t} e^{-i(\delta^2/2\beta)t[1 - \sin(2\beta t)/(2\beta t)]} e^{-(\delta^2/2\beta^2)\sin^2 \beta t} \quad (2)$$



when  $(\delta/\beta)^2$  is treated as a small expansion parameter. For free-flight times  $t$  and magnetic fields  $B$  such that  $\beta t \geq \pi$ , this amplitude contains the energy factor  $\exp[-iM_+(\beta)t]$ , leading to a nonrelativistic laboratory energy

$$E_+ = p^2/2m + \beta [1 + \delta^2/(2\beta^2)]. \quad (3)$$

The relative phase  $\phi_+(B)$  of coalescing wave fronts of an initial  $|n+\rangle$  in an interferometer with a field  $B$  present over a distance  $\ell$  in one leg (and much reduced fields elsewhere) satisfies

$$d\phi_+/dB = g\mu_N(\ell m/p) [1 - \delta^2/(2\beta^2)]. \quad (4)$$

Thus, there is an additional small  $B$ -dependent term in  $d\phi_+/dB$ , as a consequence of  $\delta$ . Replacing the quantity  $(\ell m/p)$  by the classical time-of-flight  $t$  through the region of the introduced field  $B$ , one sees that observation of the effects of  $X$ -exchange requires measuring  $\phi_+$  with sufficient precision that the experimental uncertainties remain less than  $\sim \Delta\phi_+$ , where

$$\Delta\phi_+ = (\beta t)(\delta^2/2\beta^2). \quad (5)$$

For a given value of  $t$ , we can maximize  $\Delta\phi_+$  by minimizing  $B$  subject to the constraint  $\beta \geq \beta_C = \pi/t$ , which is implied in the discussion following Eq. (2).

I have also considered spin resonance as a means of determining  $\delta$ . One measures  $\omega = E_+ - E_-$  where, including the effects of  $X$ -exchange,

$$\omega = 2\beta [1 + \delta^2/(2\beta^2)]. \quad (6)$$

That is, one requires measuring  $\omega$  to a relative precision  $\Delta\omega/\omega \leq \delta^2/(2\beta^2)$ , while satisfying the condition  $\beta t \geq \pi$ . A measure of the precision attainable in the resonance technique can be found in the more recent of a long series of experiments seeking direct evidence of time-reversal noninvariance outside the neutral kaon system<sup>3</sup> by searching for an electric dipole moment ( $eD$ ) of the neutron.<sup>4</sup>  $(\Delta\omega/\omega)_{eD} \approx 4e\sigma(D)E/2\beta$  in such experiments, where  $\sigma(D)$  is the standard deviation of  $D$ .

Quite generally, for reasons of statistics, it appears that neither implementation of the energy-shift method can compete with the beam approach for detecting the antineutron directly, which is currently being pursued.<sup>1,5</sup>

1. M. Baldo-Ceolin, Workshop on Reactor Based Fundamental Physics (Grenoble, November, 1983); see also R. C. Casella, NBS Tech. Note No. 1142, p. 60 (F. Shorten, Ed., 1981).
2. For a recent review of neutron interferometry, see A. G. Klein and S. A. Werner, Rep. Prog. Phys. 46, 259 (1983).
3. J. H. Christenson, et al., Physical Review Lett. 13, 138 (1964); R. C. Casella, Phys. Rev. Lett. 21, 1128 (1968); 22, 554 (1969).
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5. R. C. Casella, to be published.

### CRYSTAL DATA

A. D. Mighell and J. K. Stalick

Two new volumes<sup>1</sup> in the Crystal Data series were published in May 1984. The fifth volume contains 11,225 entries on crystalline compounds for which data were published in the years 1975-1978. The sixth volume contains 12,339 entries for which data were published in the years 1979-1981. These books contain information on organic and organometallic compounds. Data are also included on metal complexes containing organic ligands. The volumes in the Third Edition series are used by the industrial and academic communities for identification, for phase characterization, and for many other applications in the materials sciences.

With the aid of computer programs, the data were evaluated by the Editors for self consistency and errors or possible errors are noted. For classification and identification, the unit cell parameters for each compound were transformed to a conventional cell. NBS\*AIDS83<sup>2</sup> is the principal evaluation program which was used. This program not only evaluates the data but also builds a structured data base from which the books were prepared. The volumes were produced with typesetting routines which were written by the Data Systems Development Group of the Office of Standard Reference Data.

Each entry in the books consists of a tabulated line plus additional chemical and crystallographic data. The tabulated line contains the principal crystallographic data: cell edge ratio(s), cell parameters, quality indicator, space group or diffraction aspect, formula units per cell, observed, calculated, and recalculated density and an indication of the extent to which the atomic positional

coordinates have been determined. Next come the chemical name, synonym, formula, and literature reference. Additional information may include data on twinning, color, melting point, temperature of data collection, transition point, and an indication if powder data are in the original literature or if the study involves neutron data.

Each volume contains several chemical indexes and a lattice-formula index. The chemical indexes include a formula and a permuted formula, as well as a permuted compound name index. The lattice-formula index includes the reduced cell and the formula for each entry. The index is ordered on the ascending magnitude of the reduced cell parameters. This index is new and it permits the user to locate rapidly compounds in the book or to identify substances on the basis of limited crystallochemical data.

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1. "Crystal Data Determinative Tables." 3rd ed. U.S. Department of Commerce, National Bureau of Standards and the JCPDS--International Centre for Diffraction Data, Swarthmore, PA, USA (1984); Vols. 5-6.
  2. A. D. Mighell, C. R. Hubbard, and J. K. Stalick, "NBS\*AIDS80: A FORTRAN Program for Crystallographic Data Evaluation," NBS Technical Note 1141 (1981).

## IDENTIFICATION BY LATTICE MATCHING

Vicky L. Himes and Alan D. Mighell

We have written a lattice-matching program to be used in conjunction with the NBS Crystal Data File (1982) for the characterization and identification of crystalline materials. The NBS Crystal Data Center maintains a data base that contains evaluated crystallochemical data on approximately 60,000 commonly occurring materials. The data fall into the following categories: organics, organometallics, metals, intermetallics, inorganics, and minerals. There are two fundamental ways that large crystallographic data bases can be used. As a source of critically evaluated data, the data base can be used as a basis for scientific research, or as an aid to scientific research (i.e. to identify unknown compounds, to locate certain molecules, to obtain bibliographic data, etc.). The type of data that can be obtained through search and retrieval programs include chemical name and formula, cell parameters and cell volume, crystal system, space group symbol and number, density, bibliographic data, plus additional data. Since the data base is formatted, many of these data items may be searched readily using systems software available at a particular institution. However, general systems software will not be adequate for certain types of information search and retrieval operations. One such example is the identification of unknown compounds by matching unit cell parameters and, if available, some chemical data. Although simple in principle, lattice-formula matching is a complex operation that requires specialized scientific background in order to design a practical computer search algorithm. The following section summarizes the lattice-matching technique developed at NBS. It is planned to incorporate the formula-matching operation in a subsequent version of this program.

Three relatively recent developments have given the lattice-formula method for compound identification great potential as a routine analytical tool. First, automated methods to determine a unit cell (and crystal structure) are in widespread use. For the same reason, the data base of known crystalline compounds is large and is rapidly growing. Second, new mathematical theories have practical applications in lattice-matching procedures. These procedures permit fast and effective identification in spite of certain experimental errors made in unit cell determinations. Third, advancements in computer technology have greatly increased the efficiency of search strategies through direct access of computer file records and increased mass storage capability.



## 1. Background and Theory

The identification of materials by powder diffraction is a well-established analytical technique. With the powder method, identification is based on matching the many diffraction positions and intensities with those of known materials. In contrast, the method described herein identifies materials based on their crystalline lattices as defined by the unit cell parameters. In theory, matching unit cell parameters is equivalent to matching the positions of the diffraction lines (d-spacings) in a powder pattern. Practically, however, there are many advantages to the lattice-matching approach, mainly due to the very compact nature of the unit cell as compared to a powder pattern. For example, it is far easier to treat the experimental errors when matching unit cell parameters than it is to evaluate the errors in all the observed (and unobserved) diffraction positions in a powder pattern. In addition, the computer search times and mass storage requirements are significantly decreased since there are fewer search parameters for the lattice-matching method. Finally, with a given unit cell, mathematical procedures allow one to calculate derivative unit cells which could result from certain errors made by the experimentalists. Since the lattice-matching method is efficient, one is able to routinely search the data base of known materials for the experimentally determined unit cell as well as for its calculated derivative cells.

There are many unit cells that can be chosen to define a crystalline lattice. When identifying a material using the powder method, unique sets of data are matched since any unit cell defining the lattice gives the same calculated d-spacings. With the lattice-matching method, this uniqueness is guaranteed by always comparing reduced cells. The reduced cell is a unique, primitive cell based on the three shortest lattice translations and satisfying a specified set of mathematical conditions (International Tables for X-ray Crystallography, 1969). For identification, each unknown cell and, if desired, its associated derivative cells (Santoro & Mighell, 1973) are transformed to a reduced cell. These reduced cells are then checked against a reduced cell data base of known materials.

The NBS Crystal Data Center has prepared a data base designed for compound identification and characterization. In the NBS Crystal Data File, all known cells have been transformed to a reduced cell and the File has been sorted first on increasing magnitudes of the unit cell parameters. With this classification scheme, metrically similar lattices are located near each other in the File, making it possible to design efficient lattice-search algorithms.

A summary of the lattice-matching procedure is presented in Figure 1. From the unknown crystal, one determines a unit cell in reciprocal space. Next, a unit cell in direct space is determined and reduced. The reduced cell is then checked against a file of known materials. If desired, one calculates derivative lattices which are also reduced and checked against the file of knowns. This check can be carried out either by hand using a printed listing of knowns, or by computer programs. Practical examples of this identification procedure are illustrated in Figures 2 and 3.

In Figure 2, only one single crystal of the sample was available. Thus, a chemical analysis was not possible and a powder pattern could not be taken. The initial cell was determined on an automated diffractometer. This C-centered cell was transformed to a primitive cell and reduced. The reduced cell was then checked against the NBS Crystal Data File. The sample was found to be sodium sesquicarbonate by a direct match of the reduced cell parameters. A full structure determination by neutron diffraction confirmed the identification (Choi and Mighell, 1982).

The example given in Figure 3 shows how an identification can be made by using a derivative lattice procedure. In diffraction work, one may determine a supercell or subcell rather than the correct cell of the lattice. For example, when using powder methods, a supercell in direct space may be determined if one does not find the smallest cell consistent with the set of d-spacings. In single-crystal work, a subcell in direct space is determined if reciprocal lattice nodes are missed on a diffraction photograph or a diffractometer. In either case, it is possible to systematically calculate derivative cells and identify the material. Here, the unknown cell was correct and the known cell was a supercell. The initial cell and space group were determined on a single-crystal diffractometer and a full set of diffraction data was collected. The empirical formula was known. When checked against the file of known compounds, there were no matches. Next, the seven supercells of twice the volume were calculated; only three were unique because the initial cell is metrically rhombohedral. One of the three calculated supercells matched a cell in the NBS Crystal Data File. The known cell, which was a supercell of the correct cell, had been determined from limited powder data only. Nevertheless, it was possible to verify the correct composition and to find appropriate literature references.

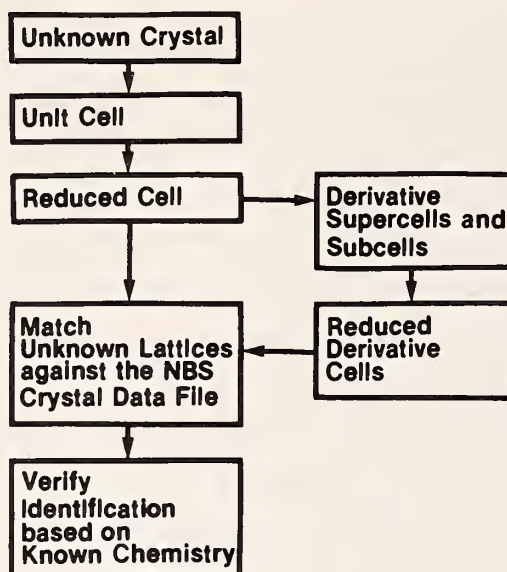


Figure 1. Identification by lattice matching.

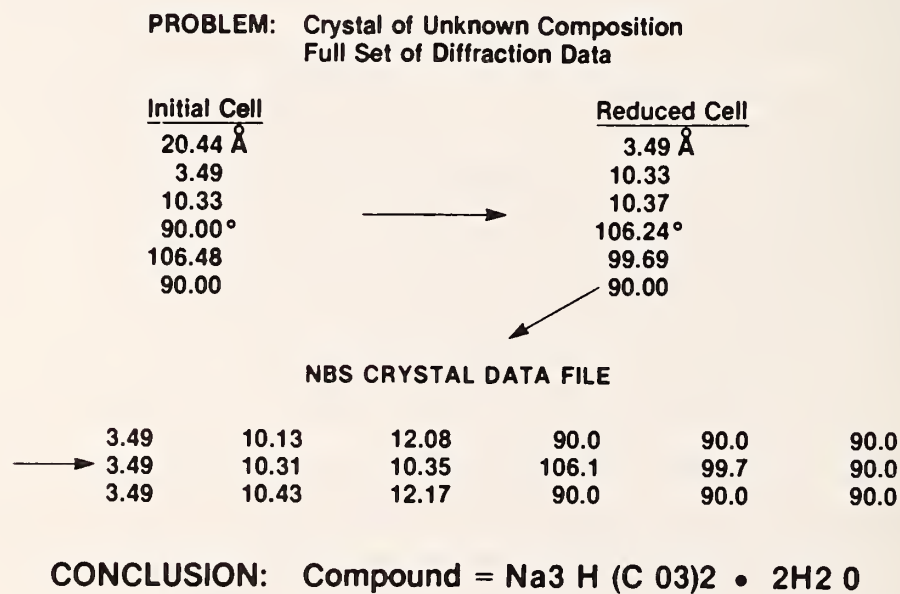


Figure 2. Identification: direct cell match.

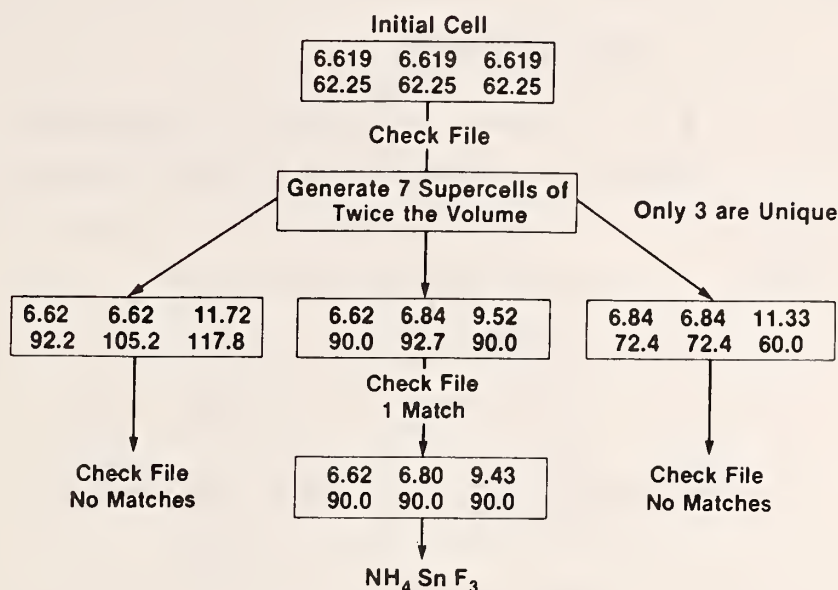
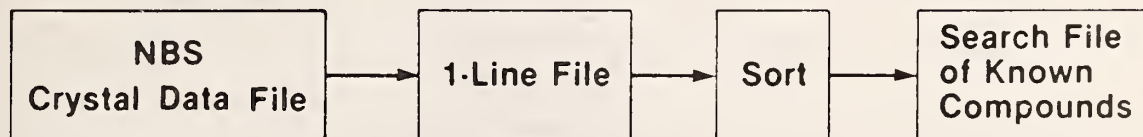


Figure 3. Identification: match of a derivative cell.

## 2. Algorithm

The theoretical basis for identification by lattice-formula matching was discussed previously. Here, emphasis is placed on the computer strategy used to match the unknown lattice(s) against the NBS Crystal Data File. Steps 1 to 4 outlined below summarize this procedure.

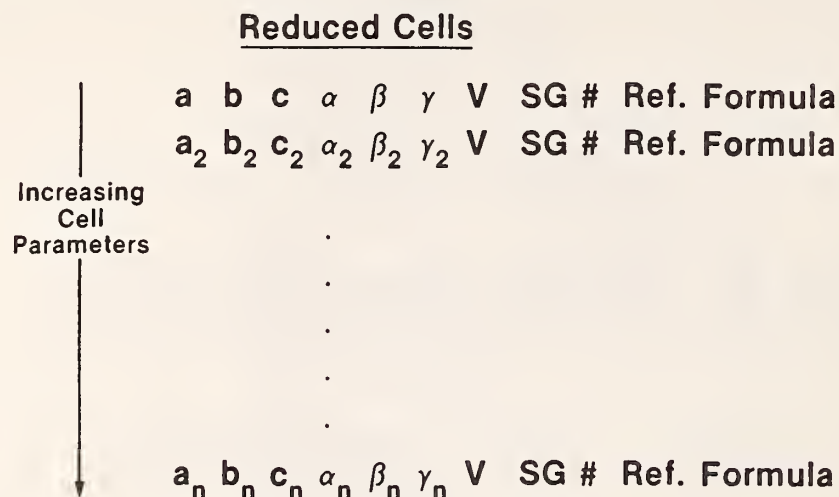
### a. Preparation of a search file of known compounds.



Before using the NBS lattice-matching program, a compact search file of known compounds must be prepared. This is done to save computer mass storage, to increase the efficiency of a search, and to simplify the program's input and output operations. Selected data from the NBS Crystal Data File are used to create a search file in which each line of 132 characters corresponds to the data for one crystalline compound. For a given computer, the 1-line search file is prepared only once.

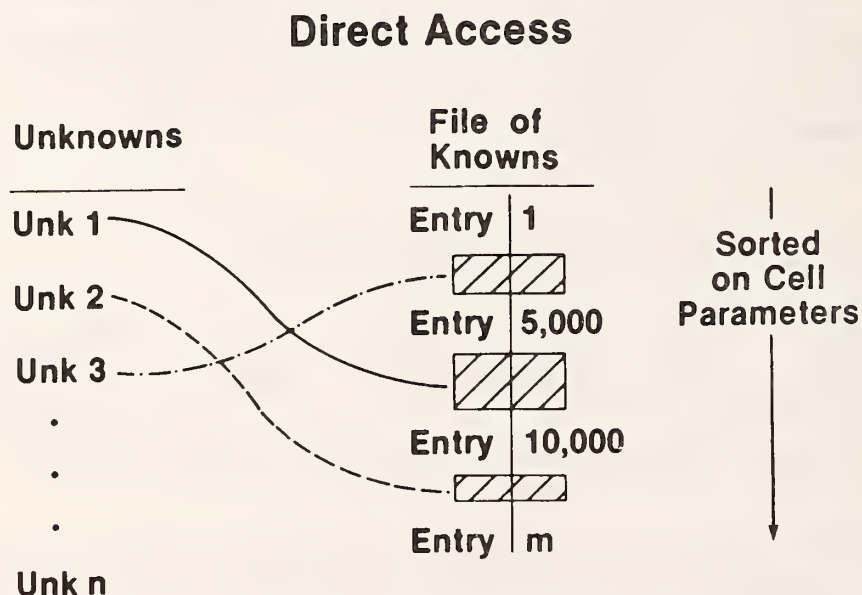


b. Data items in the search file of known lattices.



In the 1-line search file, each unknown lattice, regardless of its original centering, is represented by its primitive, reduced cell. The entries are ordered by increasing magnitudes of the reduced cell parameters. The space group, literature reference, chemical formula and other information are included in order to facilitate identification.

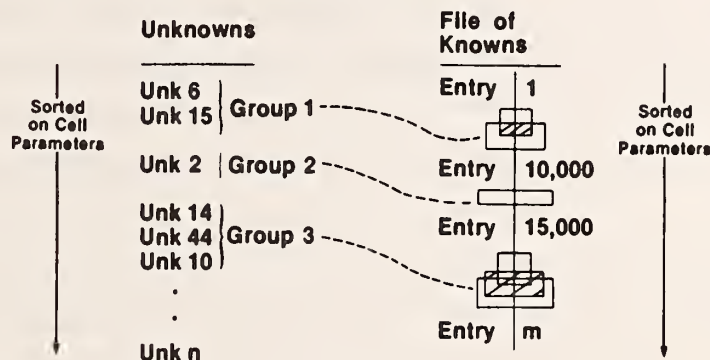
c. Search strategy.



The 1-line search file used for identification is a direct access computer file. Unlike sequential access files in which one may read only from the beginning to the end in a forward manner, direct access enables one to go directly to a specified point in the file. One can access the file in any order, "forwards" or

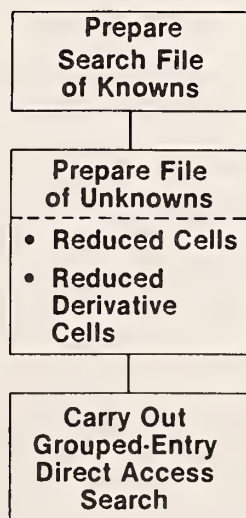
"backwards". The direct access of file records is efficient as it can significantly decrease the number of file reads. In this direct access code, a knowledge of the data in the file of knowns is used to set up a system of pointers which allows the program to start searching in about the right region of the data file. A sequential search is used only for the regions of the file in which a match is possible. In the diagram, the search regions are designated by boxes.

### Grouped-Entry Direct Access



A "grouped-entry" direct access search strategy is actually used in the computer program. To carry out a grouped-entry direct access search, the unknowns are first sorted on increasing values of the reduced cell parameters. Next, unknown cells with similar values of a (A) are searched as a group against the appropriate region of the data file. In the diagram, the regions that overlap are searched only once. This approach is very efficient when one searches a number of unknowns against the 1-line search file.

### Grouped-Entry Direct Access Search



The above diagram summarizes the lattice-matching procedure developed at NBS. First, the 1-line search file of knowns is prepared from the NBS Crystal Data File. For a given computer, this direct access file of knowns is prepared only once. Second, the file of unknowns is prepared. Each input cell may be a primitive or centered cell of the lattice. Derivative supercells and subcells may be calculated from the input cell. All cells in the file of unknowns are reduced and sorted on increasing values of the reduced cell parameters. Third, the grouped-entry direct access search is carried out. Each unknown cell as well as derivative supercells and subcells may be matched against the file of knowns in a single run.

### 3. Lattice-Matching Based on $a, b, c, V$ and Future Modifications of the Computer Program

The identification of unknown materials by lattice-matching is possible because all input cells are transformed to the standard, reduced cell. Reduction is a mathematical procedure that leads to a unique cell in all cases, provided there is no experimental error in the unit cell parameters. However, occasionally, the computer program may yield a geometrically reduced cell that requires further reduction with respect to the cell angles because of the interactions of the experimental errors with the special conditions for reduction. Thus, in practice, two experimentally determined cells defining the same lattice will always give the same  $a, b, c$  (within experimental error) for the reduced cell, but in certain cases, the reduced cell angles may differ. For this reason, the program matches only the cell edges and cell volume of each unknown reduced cell against the known cells in the NBS Crystal Data File. It is possible that every cell match obtained in this way does not define the same lattice. In the next version of the program, a mathematical procedure (Santoro, Mighell, and Rodgers, 1980) will be used to distinguish between lattices that have only  $a, b, c, V$  in common and lattices that are identical. For those cases in which more than one match of  $a, b, c, V$  occurs, knowledge of the empirical formula or some other chemical information is almost always sufficient to eliminate unwanted matches. This chemical screening will be automated in a later version of the computer program, completing the identification procedure by lattice-formula matching.

### 4. Concluding Remarks

The NBS lattice-matching procedure is reliable as one is commonly working with well-characterized materials. The cells have usually been refined by least-squares techniques and the chemistry is precisely known. The method of lattice-matching is



selective. In general, there are relatively few matches per unknown when using tolerances of  $\pm 0.1$  Å on the cell edges and  $\pm 10$  percent for the cell volume. For most crystals, the lattice is unique. This means that the cell or the cell plus some chemical data is sufficient for identification.

The lattice-formula method of identification is a general procedure that may be applied to any cell regardless of the techniques used for its determination, including single crystal, powder, and film technique. For example, the method can be applied to a compound analyzed by powder diffraction. One can index the powder pattern and search the NBS Crystal Data File. If no matches are found, one can then check the JCPDS Powder Diffraction File using a more complicated search technique based on matching d-spacings and diffraction intensities.

Lattice-matching methods are subject to precise mathematical procedures and a high degree of computerization. They are fast, selective, and various types of inter- and intra-lattice relationships can be established. Experience with practical problems has shown that identification by matching reduced cells is very straightforward and reliable when the correct cell of the lattice has been determined. However, a material can often be identified even if an error has been made in which a derivative cell of the unknown has been found. The ability to check routinely for matches of 110 extra derivative cells for each unknown is only possible because of the efficiency of the computer program and the selectivity of the method. Finally, the entire identification procedure can be highly automated including the determination of the unit cell. Both the unit cell determination and the identification process can be carried out in one instrument.

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NEUTRON ACTIVATION AUTORADIOGRAPHY STUDY OF PAINTINGS

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and

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The neutron activation autoradiography project has progressed along three fronts during the past year. The design of the facility to be located at the thermal column portion of the reactor has been finalized and an engineering detailing study is soon to begin to produce construction drawings so a more accurate estimate of the cost can be obtained. Three paintings by American artists and one by an old master were studied using the existing thermal column facility.

The first painting may be attributed to the artist Ralph A. Blakelock. The result of the autoradiography study exemplifies the uniqueness of this technique. The painting on canvas was removed from its stretcher prior to the study, in this case, as the painting had been relined in the course of conservation treatment and was removed from the stretcher for that purpose. More generally the painting is activated on the stretcher. The x-ray radiograph of the painting revealed only the canvas weave and perhaps the heavy ground layer. Nine neutron-induced autoradiographs of the painting were taken. The most prominent elements responsible for the imaging of autoradiographs 1, 6, and 9 are shown in Table 1. The relative strength of each element is normalized to the most prominent one in the same autoradiograph so one can readily follow the changes in relative strength of different elements from one autoradiograph to another. These autoradiographs demonstrate the unique capability of this technique; it allows one to see the spatial distributions of different elements separately and even to quantify them. For instance, in autoradiograph 6, pigments containing sodium and arsenic have left an entirely different picture from what is on the painting surface, a still life object painted sideways. This type of information is important to art conservation and art history study and cannot be obtained by any other conventional means. Autoradiograph 9 is also interesting. Though Zn was the most prominent element that was still active at the time, the fact that one did not see any images of the surface painting, the landscape, before autoradiograph 9 indicates that it was mercury that was responsible for the image. Zn has an isotope with a shorter half-life that was very active in the few earlier autoradiographs. Had it been Zn that was imaging the

landscape scene in autoradiograph 9, one would have been able to detect it on earlier autoradiographs as well.

The other two American paintings, the "Duet" and the "Nude", are attributed to Thomas W. Dewing. T. W. Dewing received classical training in Europe and in later years changed his style to impressionism. The "Duet" differs markedly from a photograph of the painting found in a 1924 reference. The difference typifies the changes in style. Wishing to be known as an impressionist, the artist appears to have repainted his earlier paintings to conform to his new style. Though no earlier photograph is available for the "Nude," there are studio paintings of similar period indicating his earlier style. The autoradiographs of both paintings do show that they have been reworked. These two paintings are part of a continuing effort to systematically study Dewing's works.

The fourth painting studied was a painting by a 17th century Dutch master. The study was in collaboration with the New York Metropolitan Museum of Art where a number of old master paintings have been studied using the Medical reactor at Brookhaven National Laboratory. The autoradiography study can provide information concerning the artist's style, technique, construction of painting images and type of pigments used. This information then becomes an integral part of an interdisciplinary study of the art history of the said artist.

The third area that we have devoted our effort to is in the understanding of film response to beta and gamma radiations. This will enable us to interpret the autoradiographs more accurately and also will help in identifying the most effective film system among the different film and scintillation screen combinations. The last information is important in that one is always concerned with the possible radiation effect on the painting studied with this technique, and a more efficient system to record the autoradiographs will in direct proportion reduce the amount of radiation the painting receives. Table 2 shows the number of disintegrations from gold foil needed to register a density of 1 D on the different film-screen systems. Currently, the Kodak DEF film is used without a scintillation screen for the autoradiography process. Table 2 indicates that the Kodak XAR film coupled with DuPont Quanta III screen gives the fastest response, almost a factor of 8 improvement over the current DEF system alone. Prolonging the film development time from the standard five minutes to ten minutes further improves the speed by another factor of 3.5. Thus if all these speed improvements can be realized, one can reduce the radiation the painting receives for the autoradiography study to a level less than what it would receive in a typical x-ray examination. The preliminary result indicated there would

be a trade off in degradation of image resolution with the increase of film speed. Further effort is being spent to lessen the negative effect.

Table 1

| <u>Autoradiograph<br/>No.</u> | <u>Time After<br/>Activation</u> | <u>Film Exposure<br/>Time</u> | <u>Prime Elements Exposing Film<br/>Element</u> | <u>Relative Strength</u> |
|-------------------------------|----------------------------------|-------------------------------|-------------------------------------------------|--------------------------|
| 1                             | 5 min.                           | 5 min.                        | Mn                                              | 100                      |
|                               |                                  |                               | Cu                                              | 31                       |
|                               |                                  |                               | Na                                              | 14                       |
|                               |                                  |                               | V                                               | 4                        |
| 6                             | 17 hrs.                          | 17 hrs.                       | Na                                              | 100                      |
|                               |                                  |                               | Zn                                              | 65                       |
|                               |                                  |                               | As                                              | 17                       |
|                               |                                  |                               | Mn                                              | 10                       |
| 9                             | 11 days                          | 24 days                       | Zn                                              | 100                      |
|                               |                                  |                               | Hg                                              | 5                        |
|                               |                                  |                               | Cr                                              | 3                        |

Table 2

| <u>Kodak Film Type</u> | <u>Scintillation Screen Type</u> | <u>No. of Disintegrations Needed<br/>to Register a Film Density of ID</u> |
|------------------------|----------------------------------|---------------------------------------------------------------------------|
| OH                     | Kodak Standard                   | $2.44 \times 10^6$                                                        |
| OG                     | Kodak Standard                   | $4.15 \times 10^6$                                                        |
| DEF                    | --                               | $3.32 \times 10^6$                                                        |
| DEF                    | DuPont Quanta III                | $2.36 \times 10^6$                                                        |
| XAR                    | DuPont Quanta III                | $9.24 \times 10^5$                                                        |
| XAR                    | --                               | $6.61 \times 10^6$                                                        |



## B. Non-RRD PROGRAMS

### ACTIVATION ANALYSIS GROUP: OVERVIEW

R. Fleming

The development and application of nuclear analytical techniques for greater accuracy, higher sensitivity and better selectivity are the goals of the Activation Analysis Group. A high level of competence has been developed in reactor-based activation analysis, which includes instrumental and radiochemical neutron activation analysis (INAA and RNAA), and in LINAC-based activation analysis using photons (PAA). In addition, the group has a unique capability in neutron beam analysis with both prompt gamma activation analysis (PGAA) and neutron depth profiling (NDP). The NDP technique utilizes prompt charged particle emission to determine elemental distributions within the first few micrometers of a surface while the PGAA technique utilizes prompt gamma-ray emission to measure the total amount of an element present regardless of its location in the sample. This variety of techniques provides an arsenal of tools to address analytical problems in science and technology.

During the past year, research efforts in INAA have been directed toward extending its multielement capability by investigating short-lived activation products ( $T_{1/2} \sim 1$  sec) and epi-thermal activation analysis using shielded irradiations. The work with RNAA has continued to expand the number of elements which can be quantified at or near the theoretical limiting sensitivity of the method. Especially challenging have been gas-phase radiochemical separations which have allowed routine measurement of I-129 at the  $10^8$  atom per gram level. Work on the certification of U-235 standards has demonstrated that the precision of gamma-ray spectrometry can be achieved well below the 0.1% level. Since this counting uncertainty is the ultimate limitation on the accuracy of all activation measurements, the challenge now exists to understand and, where possible, reduce systematic biases to below this level.

During the past year there has been a continuing effort in the trace element analysis of biological materials. In addition to the ongoing work on biological Standard Reference Materials and the Pilot Environmental Speciman Bank program, several new research areas have been established. Activation analysis is being used to study the interrelationships among trace elements, bioanalytical separations and biological macromolecules. Of particular interest is a new effort employing chromium isotope dilution to measure the increase in total blood volume during pregnancy.

With the success of the Bureau's effort to establish a National Facility for Cold Neutron Research at the NBS reactor (NBSR), both of the Group's neutron beam



techniques, PGAA and NDP, will improve in sensitivity and throughput by at least a factor of one hundred. This will give the Bureau an unprecedented ability for materials analysis in metals, glasses, and semiconductors, as well as more complex matrices.

The coming year will see an upgrade of the NBSR from its present 10 MW power level to the full design power of 20 MW. This will provide a factor of two improvement in many of our activation analysis sensitivities and in all of our PGAA and NDP analysis. While this upgrade is taking place, we will install a new data acquisition system based on a VAX computer to replace the outgrown 16-bit system now in use. In addition to the control and processing of gamma-ray spectra now carried out, the enhanced computational capability will be used for substantially improving the modeling of the activation analysis process to improve its accuracy.

## BIOLOGICAL MATERIALS ANALYSIS

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During the past year there has been a continuing effort in the Activation Analysis Group on trace element analysis of biological materials. This effort has taken place in a number of subject areas, with the overall aim of improving the accuracy and precision of such analyses. Brief descriptions of selected projects are given below.

a. Biological SRMS--The Non-Fat Milk Powder (SRM 1549), reported in detail last year, has now been issued and is certified for 15 elements. In addition, SRM 2670 (Toxic Metals in Freeze-Dried Urine) was issued at normal (5 elements certified) and elevated (10 elements certified) levels. Upcoming biological SRMs to be analyzed include re-issues of wheat flour and rice flour, and an apple leaves material, intended to replace the out-of-stock Orchard Leaves SRM.

Special note: NBS Spec. Publ. 260-88 became available this year (1982 Compilation of Elemental Concentration Data for NBS Biological, Geological, and Environmental SRMs). Contact the NBS Office of Standard Reference Materials (Gaithersburg, MD 20899) for a copy.

b. Pilot Environmental Specimen Bank--The specimen bank project is continuing under reduced funding, which limits the number of biological samples (human liver and marine mussel) which are being collected, processed, analyzed, and stored. We firmly believe in the viability and importance of the specimen bank concept, and are

exploring ways to revitalize the program. Copies of the extensive 1983 report of this project, including protocols for sampling and storage of human liver tissue, and accumulated analytical data on 32 elements in human liver, are still available. Refer to NBS Spec. Publ. 656, The Pilot National Environmental Specimen Bank: Analysis of Human Liver Specimens.

c. Total Blood Volume by INAA--An exploratory effort has been initiated on the determination of total blood volume by chromium isotope dilution, in cooperation with the National Institute of Child Health and Development. This project will explore use of the separated chromium-50 isotope as label for red blood cells to determine the change in total blood volume of pregnant women. This use requires the accurate determination of chromium-50 in the low ng/g range in whole blood. If successful, blood volume measurements may provide a mechanism for identifying a high risk infant mortality population.

d. Trace Elements in Brain Tissue--In a continuing cooperative effort with the Southern Illinois University School of Medicine, analyses of selected brain tissues are being used to assist in the diagnosis (postmortem) of Hallervorden-Spatz Syndrome. This is a rare brain disorder which affects childhood development and involves central nervous system degeneration. Analyses to date, including both human and monkey brain tissues, suggest that high concentrations of iron are deposited in the globus pallidus portion of the brain of affected persons. NMR studies of the iron in these tissues are currently in progress elsewhere, with additional trace element analyses to be made to further elucidate the mechanism of production and ultimate impact of these deposits.

e. Bioanalytical Separations--Interrelationships among trace elements, biological macromolecules, in-vivo and in-vitro mechanisms, and bioanalytical separations are being investigated with the use of high sensitivity instrumental and radiochemical neutron activation analysis. Among the systems being studied is the behavior of selenium and other trace elements in the glutathione peroxidase system under the influence of medication. Other investigations include the accurate determination of selenium in  $10^{-12}$  MOL of transfer-ribonucleic acid.

## MULTIELEMENT ANALYSIS OF AN AQUATIC ACCUMULATOR

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and

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A joint research program, involving the National Bureau of Standards and the Environmental Protection Agency, has been concerned with the study of biological specimens as monitors of the environment. Several analytical techniques have been used to determine over 40 elements in selected specimens. In determining elemental concentrations in biological specimens, steps were taken to assure the accuracy of the reported measurements not only in the chemical analyses, but also during sampling and sample preparation. This was especially important for elements occurring at trace levels, such as pollutant elements.

The organism selected as the monitor for the marine environment was Mytilus edulis, the marine mussel. Six thousand mussels were collected at a site in Narragansett Bay, R.I., under controlled sampling conditions. The animals were separated into batches and stored. Before analysis, the mussels were shucked and then homogenized. An instrumental approach was applied to the analyses, employing three techniques in sequence; backscatter with fundamental parameter x-ray fluorescence (BFP-XRF), neutron-capture prompt gamma activation analysis (PGAA), and instrumental neutron activation analysis (INAA). A radiochemical neutron activation analysis procedure, specific for tin, was also applied after the instrumental analyses were completed. The results of these techniques were combined to obtain concentrations for a total of 44 elements. The same 300 mg portion was analyzed in sequence by all three instrumental techniques using this scheme.

In order to analyze small subsamples that represent the bulk sample, a thorough homogenization procedure was necessary. This was accomplished with a cryogenic homogenization technique<sup>1</sup>. Possible contamination, arising from the sampling, storage, and homogenization, was evaluated by analyzing high purity water treated in the same manner as the biological samples. The results of this evaluation are shown in Table 1. Control samples, blanks, and samples of the reagents used for the final cleaning of the Teflon mills and implements used in subsampling are included for comparison. The data indicate that trace levels of contamination resulting from the sampling and subsampling processes do occur for some elements. Although these values are above the measured reagent and bag blank levels, they are still much lower than

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Table 1. Evaluation of Contamination in the Sampling and Homogenization Procedure  
Analysis by INAA (Concentrations in ng/mL, Uncertainties are 1s for n = 3)

|    | Ultrapure Water<br>Homogenate & Bag | Ultrapure Water<br>& Bag | Pure Ethyl<br>Alcohol & Bag | Commercial<br>Ultrapure Water<br>& Bag | Bag<br>Blank <sup>a</sup> |
|----|-------------------------------------|--------------------------|-----------------------------|----------------------------------------|---------------------------|
| Cr | 18 ± 4                              | 11.0 ± 0.2               | 10.8 ± 0.6                  | 11.0 ± 0.8                             | 11.1 ± 0.4                |
| Fe | 32 ± 10                             | 2.3 ± 0.3                | 7.2 ± 1.0                   | ≤ 3                                    | 3.8 ± 1.5                 |
| Co | 0.044 ± 0.010                       | 0.023 ± 0.005            | 0.015 ± 0.003               | 0.043 ± 0.010                          | 0.017 ± 0.006             |
| Zn | 25 ± 3                              | 13 ± 4                   | 11.0 ± 0.2                  | 7.6 ± 0.2                              | 7.0 ± 1.3                 |
| As | 0.035 ± 0.010                       | 0.023 ± 0.005            | ≤ 0.06                      | 0.060 ± 0.010                          | ≤ 0.010                   |
| Se | 0.030 ± 0.020                       | ≤ 0.020                  | ≤ 0.014                     | 0.020 ± 0.010                          | 0.015 ± 0.007             |
| Br | 0.89 ± 0.07                         | 0.33 ± 0.02              | 0.56 ± 0.01                 | 0.34 ± 0.04                            | 0.24 ± 0.02               |
| Mo | 0.2 ± 0.1                           | 0.043 ± 0.005            | ≤ 0.030                     | ≤ 0.07                                 | ≤ 0.03                    |
| Ag | 0.029 ± 0.003                       | 0.45 ± 0.20              | 0.064 ± 0.010               | 0.074 ± 0.030                          | ≤ 0.009                   |
| Cd | 0.34 ± 0.04                         | 0.086 ± 0.010            | ≤ 0.060                     | ≤ 0.16                                 | ≤ 0.30                    |
| Ce | 0.075 ± 0.015                       | 0.021 ± 0.003            | ≤ 0.010                     | 0.030 ± 0.008                          | 0.022 ± 0.006             |
| Hg | 0.59 ± 0.07                         | 0.115 ± 0.011            | 0.112 ± 0.005               | 0.16 ± 0.08                            | 0.099 ± 0.007             |

<sup>a</sup> Apparent concentration for a 50 mL sample.



Table 2. Elemental Concentrations (Dry Weight Basis) for Mytilus edulis  
(Concentrations in  $\mu\text{g/g}$  unless otherwise specified)

|        | Concentration $\pm$ 1s Analytical<br>Uncertainty | Techniques Employed                     |  |
|--------|--------------------------------------------------|-----------------------------------------|--|
|        |                                                  | (a = XRF, b = PGAA, c = INAA, d = RNAA) |  |
| H (%)  | 5.9 $\pm$ 0.9                                    | b                                       |  |
| B      | 31 $\pm$ 2                                       | b                                       |  |
| C (%)  | 62 $\pm$ 12                                      | b                                       |  |
| N (%)  | 7.6 $\pm$ 1.8                                    | b                                       |  |
| Na (%) | 5.65 $\pm$ 0.06                                  | b,c                                     |  |
| Mg (%) | 0.69 $\pm$ 0.06                                  | a                                       |  |
| Al (%) | 0.074 $\pm$ 0.003                                | a,c                                     |  |
| Si (%) | 0.300 $\pm$ 0.010                                | a                                       |  |
| P (%)  | 0.900 $\pm$ 0.013                                | a                                       |  |
| S (%)  | 2.2 $\pm$ 0.2                                    | a,b                                     |  |
| Cl (%) | 10.0 $\pm$ 0.2                                   | a,b,c                                   |  |
| K (%)  | 1.4 $\pm$ 0.3                                    | a,b,c                                   |  |
| Ca (%) | 0.54 $\pm$ 0.04                                  | a,c                                     |  |
| Sc     | 0.130 $\pm$ 0.006                                | c                                       |  |
| V      | $\leq 2$                                         | c                                       |  |
| Cr     | 2.2 $\pm$ 0.5                                    | c                                       |  |
| Mn     | 28 $\pm$ 3                                       | a,c                                     |  |
| Fe     | 475 $\pm$ 30                                     | a,c                                     |  |
| Ca     | 0.494 $\pm$ 0.013                                | c                                       |  |
| Ni     | 3.3 $\pm$ 0.3                                    | a                                       |  |
| Cu     | 6.7 $\pm$ 0.6                                    | a,c                                     |  |
| Zn     | 122 $\pm$ 3                                      | a,c                                     |  |
| As     | 11 $\pm$ 1                                       | a,c                                     |  |
| Se     | 2.65 $\pm$ 0.04                                  | a,c                                     |  |
| Br     | 430 $\pm$ 10                                     | a,c                                     |  |
| Rb     | 8 $\pm$ 1                                        | a,c                                     |  |
| Sr     | 75 $\pm$ 3                                       | a,c                                     |  |
| Mo     | 1.4 $\pm$ 0.3                                    | c                                       |  |
| Ag     | 0.691 $\pm$ 0.010                                | c                                       |  |
| Cd     | 2.2 $\pm$ 0.3                                    | b,c                                     |  |
| Sn     | -                                                | d                                       |  |
| Sb     | 0.019 $\pm$ 0.004                                | c                                       |  |
| Cs     | 0.061 $\pm$ 0.003                                | c                                       |  |
| Ba     | 6.9 $\pm$ 1.5                                    | c                                       |  |
| La     | 0.056 $\pm$ 0.010                                | c                                       |  |
| Ce     | 0.89 $\pm$ 0.08                                  | c                                       |  |
| Sm     | 0.096 $\pm$ 0.011                                | c                                       |  |
| Eu     | 0.018 $\pm$ 0.002                                | c                                       |  |
| Hf     | 0.060 $\pm$ 0.003                                | c                                       |  |
| Au     | 0.360 $\pm$ 0.010                                | c                                       |  |
| Hg     | 0.23 $\pm$ 0.09                                  | c                                       |  |
| Pb     | 4.3 $\pm$ 0.7                                    | a                                       |  |
| Th     | 0.118 $\pm$ 0.009                                | c                                       |  |
| U      | 0.185 $\pm$ 0.020                                | c                                       |  |

---

\*  
d Radiochemical neutron activation analysis technique in progress.

the measured concentration in the mussel tissue and do not make significant contributions to the concentrations.

Utilizing the combination of techniques (XRF, PGAA, INAA, and RNAA), the mussel tissue was analyzed for a total of 44 elements. The compiled results for one mussel batch can be seen in Table 2. Some slight differences among results were found in the sequential analysis procedure. The causes for those differences will be evaluated, employing the quality control methods in place during the analyses.

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#### COMPARATIVE IRRADIATIONS AT UVAR AND NBSR

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Samples of pure silicon and of potassium iodide were irradiated at the University of Virginia Reactor (UVAR) and the NBSR in order to determine comparative values of thermal and fission flux in the two reactors. At UVAR, the samples were irradiated in the hydraulic rabbit, separated from the fuel region by a graphite element approximately 76 mm thick. The rabbit facility is of aluminum construction, flooded with water, and surrounded with graphite on three sides and with water on the side away from the core. At NBS, KI samples were irradiated in pneumatic tubes RT3 and RT4.

Irradiated silicon was assayed at UVA for Si-31 and then for Al-29 activities as outlined by Bickford and Fleming,<sup>1</sup> correcting for the different geometries used in the two measurements. The ratio of the saturated counting rates of these nuclides provides an experimental figure of merit proportional to the thermal/fast flux ratio which is independent of the detector calibration and of the nuclear parameters, some of which are poorly known. The saturated activity ratio  $A(31)/A(29)$  at UVAR is 0.18; for comparison, Bickford and Fleming reported 9.51 for RT4 and 0.74 and 0.83 for the G2 and G4 in-core positions, respectively.

Samples of KI irradiated at both reactors were assayed for K-42 and I-126 activity after a week's decay. Using thermal and fission-spectrum cross sections from the IAEA tabulation,<sup>2</sup> correcting counting efficiency for gamma energy, and

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normalizing to the published thermal flux in RT4,<sup>3</sup> the thermal and fission-spectrum fluxes are as follows:

| Facility | Sample | Thermal flux | Fission flux |
|----------|--------|--------------|--------------|
| UVAR     | Si     | --           | 1 E 12       |
| UVAR     | KI     | 1.2 E 13     | 2 E 12       |
| RT3      | KI     | 4.9 E 13     | 3 E 12       |
| RT4      | Si (1) | --           | 2 E 10       |
| RT4      | KI     | --           | 9 E 10       |

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## NITROGEN CONCENTRATION DISTRIBUTIONS BY NEUTRON DEPTH PROFILING

J. T. Maki, R. G. Downing, and R. F. Fleming  
(Inorganic Analytical Research Division)

Neutron depth profiling (NDP) at the NBS facility<sup>1</sup> has been successfully carried out for He-3, Li-6, B-10, and Na-22, each of which has a reaction cross section of ~ 1000 barns or more. The profiling of nitrogen concentrations using the  $^{14}\text{N}(n,p)^{14}\text{C}$  reaction is much more difficult since the cross section for 2200 m/s neutrons is only 1.8 barns. However, with special attention to background reduction, nitrogen profiling has been accomplished using the BT-3 thermal neutron beam at the 10 MW NBSR. The increase of reactor power to 20 MW will improve NDP sensitivity by a factor of two, while the NBS Cold Source/Guide Hall facility would provide at least a 100 times improvement.

The nitrogen profiling measurements were made using two samples, a silicon nitride ( $\text{Si}_3\text{N}_4$ ) layer on a silicon wafer, and an ion-implanted tungsten carbide-cobalt<sup>4</sup> alloy. The  $\text{Si}_3\text{N}_4$  layer was 50 nm thick corresponding to  $3 \times 10^{17}$  N-14 atoms per  $\text{cm}^2$  and was found to have an overcoating of ~ 500 nm of  $\text{SiO}_2$ . The WC alloy had been ion-implanted at 90 keV to a dose of  $5 \times 10^{17}$  N-14 atoms per  $\text{cm}^2$ . Thus, both samples were close to the estimated nitrogen sensitivity of  $1.8 \times 10^{17}$  atoms/ $\text{cm}^2$ .<sup>1</sup>

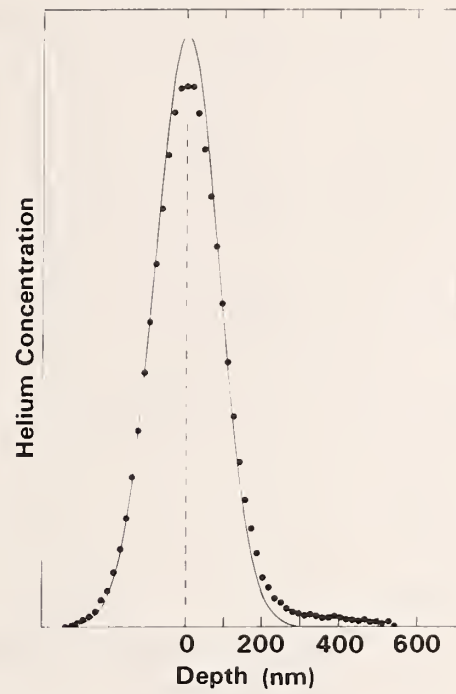


Figure 1. Depth profile of a helium surface layer on aluminum: concentration profile (---), convoluted profile (—), measured data (●).

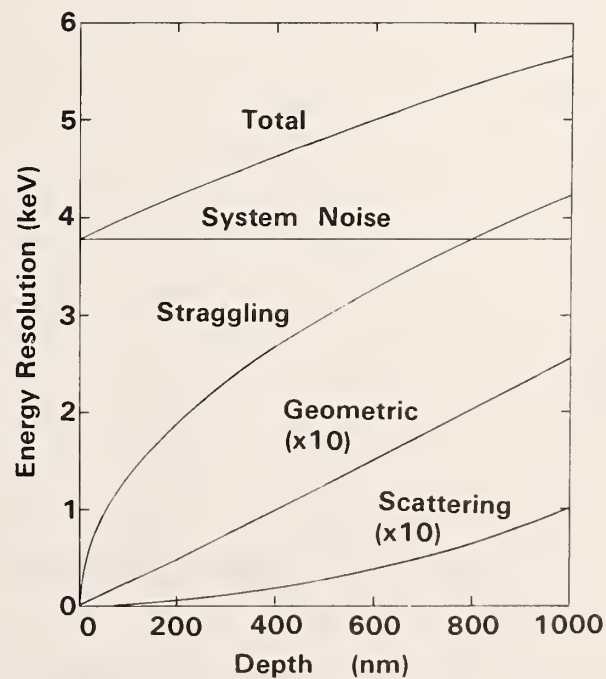


Figure 2. NDP energy resolution for nitrogen in silicon dioxide.



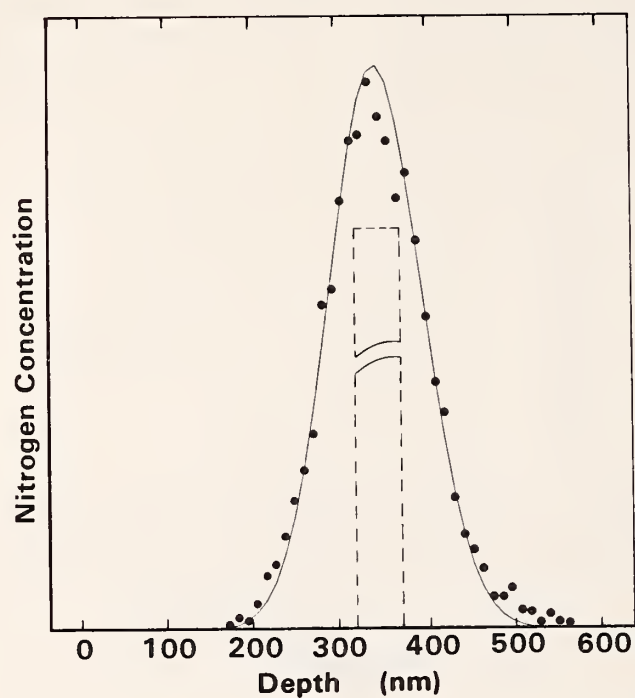


Figure 3. Nitrogen depth profile of a 50 nm layer of  $\text{Si}_3\text{N}_4$  on a silicon wafer: concentration profile (---), convoluted profile (—), measured data (●).

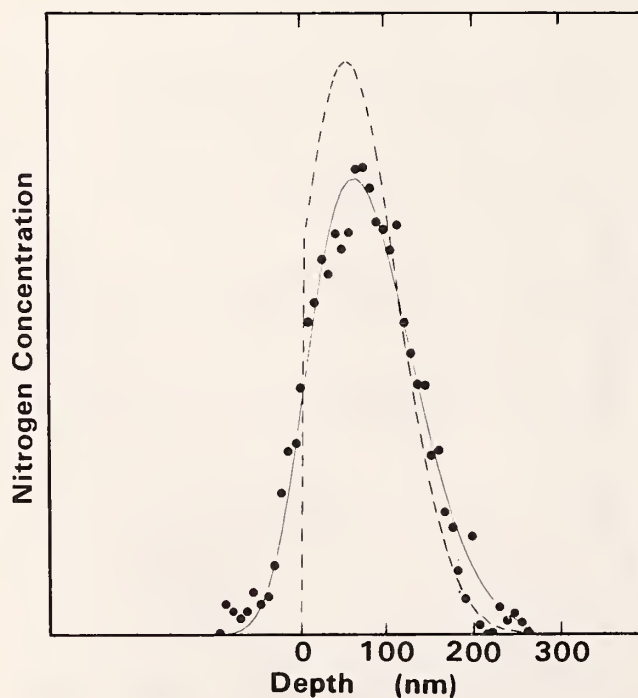


Figure 4. Nitrogen depth profile of a 90 keV implant into a WC-Co alloy to a dose of  $5 \times 10^{17}$  ions/cm<sup>2</sup>: concentration profile (---), convoluted profile (—), measured data (●).

The protons from the  $^{14}\text{N}(\text{n},\text{p})^{14}\text{C}$  reaction have an initial energy of 583.85 keV and retain an energy upon leaving the sample surface corresponding to the depth at which the reaction takes place. The measured charged particle spectrum is this distribution of degraded proton energies broadened by the measurement response function. This response function is the energy broadening caused by system noise, energy straggling, small-angle scattering, and geometrical pathlength broadening. System noise was measured by determining the peak width for a precision pulse signal, and was found to be independent of pulse amplitude. That this response function adequately represented the system noise for protons was demonstrated (see Figure 1) using a surface sample of He-3 for which the other three contributions to the response function were negligible and for which there is excellent sensitivity. The depth-dependent contributions to the response function - straggling, small-angle scattering and pathlength broadening - were calculated analogous to the work of Biersack<sup>2</sup>. The total response function at a given depth was represented as a gaussian with a width determined from the widths of the four contributions added in quadrature. For nitrogen at the depths investigated only energy straggling was significant compared to the system noise. The relative importance of the contributions to the response function are shown in Figure 2.

The convolution procedure was synthetic. An N-14 concentration distribution was assumed and the resulting pulse height spectrum was computed using the response function and the proton stopping power tabulation of Zeigler<sup>3</sup>. The goodness-of-fit was determined by minimizing the chi-squared statistic. The results for the 50 nm layer of  $\text{Si}_3\text{N}_4$  on silicon are shown in Figure 3. The assumed 50 nm layer at a depth of 320 nm of equivalent, inactive silicon nitride is shown to give a good fit to the measured data. This overcoat thickness is equivalent to 485 nm of  $\text{SiO}_2$ . Subsequent Rutherford backscattering measurement confirmed a 470 nm  $\text{SiO}_2$  cap over the silicon nitride layer. The nitrogen implantation into tungsten carbide was represented as a gaussian, truncated at the surface. Again the convoluted results, shown in Figure 4, show good agreement with the measured data. The mean implantation depth is 56 nm with a standard deviation of 58 nm for the gaussian profile.

In summary, nitrogen profiling using NDP has been demonstrated and the concentration distributions have been obtained by deconvolution. These measurements are at the sensitivity limit of the thermal neutron NDP facility at NBS taking a day or two of running time and could be improved by at least 100 times using an NDP instrument on an NBS Cold Source beam.

1. R. G. Downing, R. F. Fleming, J. K. Langland, and D. H. Vincent, "Neutron Depth Profiling at the National Bureau of Standards," Nuc. Inst. and Meth. 218, 47 (1983).
2. J. P. Biersack, D. Fink, R. Henkelmann and K. Müller, "The Use of Neutron Induced Reactions for Light Element Profiling and Lattice Localization," Nuc. Inst. and Meth. 149, 93 (1978).
3. H. H. Andersen and J. F. Ziegler, The Stopping and Ranges of Ions in Matter: Hydrogen, Volume 3, Pergamon Press, New York (1977).
4. We thank James Ehrstein of NBS for the silicon nitride sample and Daniel Oblas of GTE, Waltham, Mass. for the implanted tungsten carbide alloy.

#### HIGH ACCURACY DETERMINATION OF U-235 BY GAMMA-RAY SPECTROMETRY IN NONDESTRUCTIVE ASSAY STANDARDS

R. R. Greenberg and B. S. Carpenter  
(Center for Analytical Chemistry)

The joint project has been completed between the Central Bureau for Nuclear Measurements (CBNM), Geel, Belgium, and the National Bureau of Standards (NBS), and a set of five uranium isotope abundance reference materials for nondestructive assay (NDA) have been produced. These reference materials have been identified as NBS SRM 969 and the Commission of the European Communities certified reference material EC NRM 171 and are intended for worldwide safeguards use as primary reference materials for the determination of the U-235 abundance in homogeneous uranium bulk material by gamma spectrometry. The reference material is in the form of uranium oxide ( $U_3O_8$ ) and is placed in aluminum cans with nominal isotope abundances ( $^{235}U/U$ ) of 0.003, 0.007, 0.019, 0.029, and 0.045. The material at each isotope abundance is characterized chemically by CBNM, NBS, and the DOE New Brunswick Laboratory for  $^{235}U/U$  homogeneity and isotope abundance, uranium content, and material impurities.<sup>1,2</sup>

High precision/high accuracy gamma-ray measurements were made on 24 representative sample cans of the 140 total cans at each isotope abundance. The measurements, using a high purity germanium detector, determined the counting rate uniformity of the U-235 185.7 keV gamma-ray as well as the U-235 isotope abundance for each sample. Since the samples were packaged such that the  $U_3O_8$  was infinitely thick for the 185.7 keV gamma-ray, the measured counting rate was almost independent of the material density. In addition, the activity observed by the detector was

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collimated to simulate calibration conditions used to measure bulk material in the field.

This work, as seen in Table I, has demonstrated that it is possible to achieve a precision of 0.05% and a standard deviation of the mean of 0.01% in gamma spectrometry measurements. To obtain this level of precision, the analyst must give careful attention to the factors associated with the measurement process. If all errors are controlled and a set of well characterized standards are available, it appears that an accuracy of a few hundredths of one percent (2σ) for U-235 isotope abundance can be achieved by gamma spectrometry.

Table I. Preliminary Results for U-235 Abundances (Atom Percent) in NDA Samples as Determined by Gamma Spectrometry and Thermal Ionization Mass Spectrometry.

| Sample | This Work - GS |                    |                    |                    | NBS - MS <sup>a</sup> |       | CBNM - MS <sup>a</sup> |       |
|--------|----------------|--------------------|--------------------|--------------------|-----------------------|-------|------------------------|-------|
|        | Mean           | σ-abs <sup>c</sup> | σ-rel <sup>c</sup> | σ-rel <sup>d</sup> | Mean                  | σ-rel | Mean                   | σ-rel |
| 031    | 0.3207         | 0.0003             | 0.11               | 0.021              | 0.3207                | 0.08  | 0.3207                 | 0.05  |
| 071    | 0.7212         | 0.0005             | 0.07               | 0.015              | 0.7218                | 0.02  | 0.7208                 | 0.05  |
| 194    | 1.9666         | 0.0010             | 0.05               | 0.011              | 1.9667                | 0.02  | 1.9668                 | 0.02  |
| 295    | 2.9828         | 0.0019             | 0.06               | 0.013              | 2.987                 | 0.02  | 2.9850                 | 0.02  |
| 446    | 4.5143         | 0.0026             | 0.06               | 0.012              | n/a                   | n/a   | 4.5183                 | 0.04  |

a Preliminary values reported in reference 1.

b Absolute sample standard deviation (in atom percent of U-235).

c Relative sample standard deviation (in percent).

d Relative standard deviation of the mean (in percent).

1. P. DeBievre, H. Meyer, J. Van Audenhove, B. S. Carpenter, and J. W. Gramlich, "Progress Report on the Establishment of Uranium Isotope Abundance Reference Materials for NDA," Proceedings of The Fourth Annual Symposium--ESARDA on Specialist Meeting on Harmonization and Standardization in Nuclear Safeguards, Petten, The Netherlands, (1982).
2. R. R. Greenberg and B. S. Carpenter, "High Accuracy/High Precision Determination of U-235 in Nondestructive Assay Standards by Gamma-Ray Spectrometry," Proceedings of the Fifth International Conference on Nuclear Methods in Environmental and Energy Research, Mayaguez, Puerto Rico, (1984).



## SUMMARY OF ACTIVITIES CARRIED OUT BY THE NEUTRON FIELD STANDARDS GROUP

D. Gilliam, J. Grundl, and E. McGarry  
(Center for Radiation Research)

The Neutron Field Standards Group, attached to the Center for Radiation Research (CRR), is engaged in the development and application of standard and reference neutron fields as permanent facilities for neutron detector calibrations, neutron dosimetry standardization, and reaction rate cross-section measurement.

A component of this group's activities makes use of the reactor thermal column and the tangential beam tubes where facilities, designed and built by the Neutron Field Standards Group, are in operation. Facilities, development, and measurement programs which involve these facilities are as follows:

1. Production of Neutron Fluence Standards

The cavity fission source continued to be employed for the production of neutron fluence standards for both national and international programs of reactor pressure vessel dosimetry. For the first time this year, fluence standards for the Np and U-238 fission reactions were prepared. Eight species of fluence standards have been produced to date for materials neutron dosimetry applications:  $\text{In}(n,n')$ ,  $\text{Ni58}(n,p)$ ,  $\text{Fe54}(n,p)$ ,  $\text{Ti}(n,p)$ ,  $\text{Rh}(n,n')$ ,  $\text{Al}(n,\alpha)$ ,  $\text{U238}(n,f)$  and  $\text{Np}(n,f)$ . Fission neutron fluences certified for these standards are in the range  $0.7$  to  $60 \times 10^{14}$  neutrons/cm<sup>2</sup>.

2. Preparations for a New Neutron-Driven Gamma-Ray Standard

In cooperation with two European laboratories and the University of Virginia, preparations are underway for the construction of a high-intensity gamma-ray standard at the reactor thermal column. The basic design concept is to place thermal-neutron black absorbers, formed as nested cylinders, into the thermal column cavity. The resulting capture gamma ray source in the black absorber is directly proportional to the incident thermal neutron intensity. The gamma ray dose at the center of the cylinder from this source can be ascertained from capture gamma data, dose conversion tables, and simple geometry calculations. Goal accuracies of  $\pm 10\%$  have been set for an estimated free-field central x-ray dose of  $\sim 6\text{KGy/h}$  (14 megarads/day).

The system under construction will use initially an extruded cadmium cylinder for the gamma-source black absorber (rich in high energy gammas compared to conventional Co gamma ray standards) and a segmented cylinder of Li-6 glass for a no-gamma-source black absorber.

## NON-RRD PROGRAMS

Known Cd-gamma doses then are delivered to a detector on the basis of responses obtained with and without the Li-6 glass cylinder. The cadmium cylinder is in hand and Li-6 glass cylinders are being fabricated by the NBS Glass Research Group. A new shield plug for the thermal column door penetration also has been fabricated.

Immediate applications of the new gamma source include (1) investigation of photofission interference in U-238 fission dosimeters; and (2) calibration of a proposed Li-6 chip dosimeter for high intensity gamma dosimetry in fission reactor environments.

### 3. Calibration of Helium Accumulation Fluence Monitors (HAFM)

A neutron fluence transfer irradiation was carried out in the Intermediate Energy Standard Neutron Field (ISNF) in order to establish a neutron fluence scale for the HAFM calibration irradiations reported in last year's summary.

In this final irradiation, the absolute value of the fission rate from a well-assayed deposit of U-235 was observed during the activation of two pairs of gold and indium monitor foils. One pair of monitor foils was mounted against the platinum backing of the U-235 deposit at the center plane of an active fission chamber, while the other pair of monitor foils was mounted against the thin aluminum anode of the fission chamber. The fluence for the calibration run was derived by relating the U-235 fission rate to the corresponding fission rates observed for carefully intercompared U-235 deposits at the Cf-252 facility. Fluence rates at a well-determined distance at the Cf-252 facility are known on an absolute basis by comparison of the Cf-252 source to the standard neutron source NBS-I via the manganese bath method. Table I gives the results of the fluence determination and a list of error factors.

The last item in the error list is worth some explanation because it illustrates some of the considerable but necessary efforts required to establish a reliable standard neutron field. In the fluence calibration run which compared foil activation rates with the U-235 fission rate, the B-10 shell of the ISNF was penetrated by the stem of the fission chamber. (This penetration was not present in the HAFM calibration runs.) The penetration was closed to thermal neutrons by a cadmium flange and tube that extended out of the cavity into a region of negligible neutron flux density. Any residual thermal neutron penetration has no effect because of the background subtraction method. However, epithermal neutrons (coming from multiple scattering of the U-235 fission neutrons in the graphite) can cause a perturbation by leaking into the ISNF test region through the penetration for the fission chamber. The magnitude of this epithermal leakage perturbation has been

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assessed by two methods: (1) by adding a B-10 sleeve around the Cd tube and (2) by comparing the ratio of U-235 and U-238 fission rates in the completely closed ISNF with the ratio for the penetrated shell. The results of these assessments have been somewhat inconsistent. The addition of a B-10 sleeve around the Cd tube did not change the U-235 fission rate in the ISNF interior ( $\pm 0.3\%$ ), yet the U-235 fission rate (relative to that of U-238 was found to be  $(2 \pm 1\%)$  higher in the case of the penetrated shell. A correction factor of  $0.99 \pm 1.5\%$  has been applied to account for the epithermal penetration effect. This uncertainty is the largest single entry in the list of error factors.

TABLE 1

## FLUENCE AND IRRADIATION TIMES FOR HAFM CALIBRATION IRRADIATION

Total Central Fluence:  $1.257 \text{ E14 neutrons/cm}^2$   
 Total Irradiation Time:  $164,882 \pm 10 \text{ seconds}$

### Uncertainty Factors in Total Central Fluence:

#### Fluence Transfer Errors

|                                                        |             |
|--------------------------------------------------------|-------------|
| Cf neutron source strength                             | $\pm 0.9\%$ |
| Geometry factors at Cf-252 facility                    | $0.6\%$     |
| Scattering correction uncertainties at Cf-252 facility | $0.4\%$     |
| Cf/ISNF cross section ratios for U-235, Pu-239         | $1.6\%$     |
| Pu-239 (n,f) reaction probability at Cf                | $0.7\%$     |
| Subtotal                                               | $\pm 2.1\%$ |
| Epithermal leakage in fluence calibration run          | $\pm 1.5\%$ |
| <hr/>                                                  |             |
| Total uncertainty                                      | $\pm 2.6\%$ |

#### 4. Comprehensive Estimate of Errors in ISNF Fluence Scale

An effort is underway to establish a more complete estimate of Cf/ISNF cross section ratio errors for fission reactions used to establish the ISNF neutron fluence scale. This error component, presently quoted as  $\pm 0.3\%$  (see Table 1), takes into account only neutron spectrum uncertainties. The initial investigation of cross section errors suggests that (1) an additional  $1.5\%$  or so should be included in this fluence transfer ratio; and (2) a consensus fluence transfer involving threshold as



## NON-RRD PROGRAMS

well as non-threshold fission reactions may be preferable to the present strategy of using a single fluence transfer reaction (i.e.,  $\text{Pe-239 (n,f)}$ ).

### NEUTRON PERSONNEL DOSIMETER CALIBRATION AND TESTING

Robert B. Schwartz  
(Center for Radiation Research)

The reactor filtered beams, with energies of 2, 24, and 144 keV, together with the beam from the thermal column, were used for calibrating and testing personnel dosimeters.

In particular, a new configuration for a personnel dosimeter was calibrated in the thermal column beam for Lawrence Livermore Laboratory; dosimeters were irradiated in the keV beams as part of the work for a Master's thesis from the University of Michigan; and an improved type of track etch dosimeter was irradiated for the Centro di Studi Nucleari. This latter irradiation is potentially most significant, since track etch dosimeters represent one of the most promising developments in personnel dosimetry. Their drawback lies in the fact that their response falls off drastically in the neutron energy region below about 50 keV. This new dosimeter is supposed to respond to neutrons of 10 keV energy or lower, and thus represents a significant improvement. Our 24 keV beam is the best source of monoenergetic neutrons in this energy region anywhere in the world, and hence is essential for proving out the new technique. (As of this writing, the results of these irradiations are not yet known.)

A new line of research for our group consists of measurements with a "tissue-equivalent proportional counter." This is a counter whose gas filling has approximately the same chemical constituents as tissue (i.e., oxygen, nitrogen, hydrogen, and carbon, in the form of  $\text{CO}_2$ ,  $\text{N}_2$ , and  $\text{CH}_4$ ). By filling the counter to an appropriate pressure (typically 5 or 6 cm Hg) the counter will simulate a tissue sphere about one micron in diameter, and the interactions in the counter gas will simulate those in an actual small tissue volume. The spectra, when appropriately analyzed, can be used to determine dose and dose equivalent as a function of the energy deposited in tissue.

The first results with the 144 keV beam are shown in Figure 1. The abscissa is the quantity "lineal energy," which is the energy imparted to the "tissue," divided by the mean chord length of the (one micron diameter) tissue sphere. This quantity is called "y," with units of keV/micron. The ordinate is "y" multiplied by the



quantity " $y \cdot D(y)$ ," where  $D(y)$  is the integral absorbed dose distribution for events up to lineal energy  $y$ . When plotted on semi-log paper (as is done here) equal areas represent equal doses. The peak, at about 60 keV/micron, represents the distribution

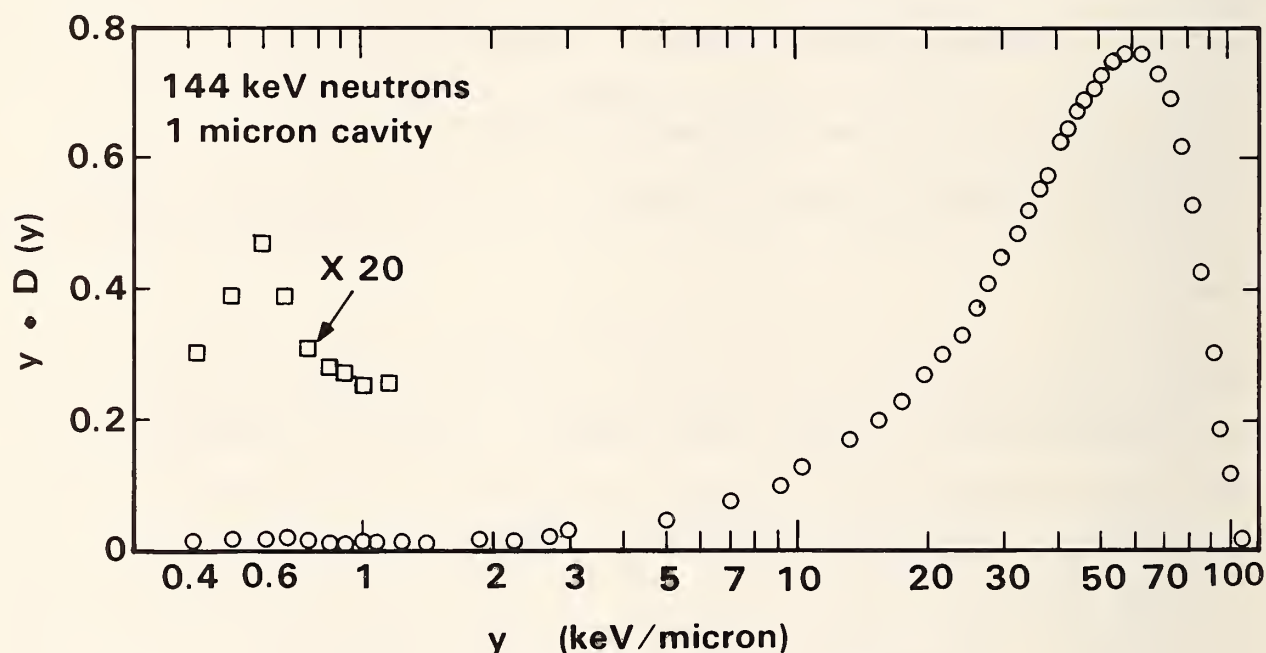


Figure 1. Microdosimetric spectrum,  $y \cdot D(y)$  vs.  $y$ , for 144 keV neutrons.

of dose due to recoil protons from the 144 keV neutrons. The small peak at about 0.6 keV/micron (data points multiplied by a factor of 20 to make the peak more visible) represents the gamma dose. This peak is real: each channel represents >100,000 counts, but there is simply very little gamma dose in this beam. The shape is in general agreement with recent calculations.

Further measurements with the other reactor beams are to be done shortly; these measurements will be compared with calculations done by other members of CRR.

## C. REACTOR OPERATIONS AND SERVICES

The reactor was operated on a normal round-the-clock schedule for the entire year. Other than scheduled shutdowns for maintenance, refueling, testing, and for staff vacation, there were no interruptions in the operating schedule. The program of modernization of reactor components and instrumentation is continuing. Licensing activities to upgrade reactor power to 20 MW and renew the operating license were completed. Extensive hearings were held before the Advisory Committee on Reactor Safeguards as the final stage in the licensing process. In May 1984, the Nuclear Regulatory Commission issued to NBS a new operating license allowing operation at 20 MW, double the existing power, and valid until the year 2004. This is a major accomplishment and a milestone in the history of the facility. It is expected that the reactor will be shut down this fall for upgrade and conversion to 20 MW. The work is expected to be completed by the end of the year and testing for 20 MW operations is to begin early in 1985.

Utilization of the reactor continued to be extensive and wide ranging. More than 125,000 instrument hours involving 25 simultaneously operable experimental facilities have been provided to more than 50 organizations from within and outside NBS.

### 1. Reactor Operations

Reactor operations continued at a high level with on-line time and fuel efficiency almost identical to that of the previous year which are among the best in the history of the facility. A summary of the overall operating statistics for the period July 1, 1983 to June 30, 1984 is presented in the following table.

NBSR Operating Summary July 83-June 84

|                       |      |
|-----------------------|------|
| No. of days at 10 MW  | 266  |
| On-line time at 10 MW | 73%  |
| Average U-235 burnup  | 62%  |
| No. of Irradiations   | 1900 |
| Hours of Irradiations | 5600 |
| Hours per Irradiation | 3    |

### 2. Irradiation Service

Heavy utilization of the reactor for major irradiation and activation analysis programs continued. Tens of thousands of specimens, involving foods, drugs, environmental monitoring, geological, and mineral examinations, forensic

## REACTOR OPERATIONS AND SERVICES

investigation, and development of standard reference materials were irradiated at the NBS reactor. Substantial quantities of fluorine-18 were produced on a regular basis in support of a new medical research program at the National Institutes of Health.

### 3. Engineering Services

In addition to normal engineering and design services provided to reactor operations, experimenters and users, the engineering staff was involved in a comprehensive program of reactor modernization.

Sixteen new reactor shim arm poison blades, arbors and bearings were completed, received, and accepted by the NBSR engineering. The shim arm blades were made previously by Argonne National Laboratory, but are no longer available from ANL since they are no longer made for the CP-5 reactor. This is the first time the blades were made commercially and new manufacturing techniques had to be developed which required a great deal of engineering and quality control procedures. The production of these blades solved one of the most difficult projects at the reactor since they must be replaced periodically. The last blades available were put in service in 1979. This accomplishment will provide NBSR with a lifetime supply of these critical components. The yokes for the shim arms have been designed and will be fabricated as the schedule allows. A shim arm test assembly is in the process of fabrication which in addition to testing shim arm mechanisms will be available as spare parts.

Qualification fuel plates have been accepted from the DOE contractor and were fabricated into fuel element assemblies. Twenty-three fuel element assemblies have been accepted by the NBSR engineering staff.

The spare regulating rod has been modified and the absorber section is being fabricated for 20 MW operation. An engineering change notice (ECN) provided an improvement in the performance of the automatic regulating rod. By applying an electric braking technique, slippage of the regulating rod was reduced to a minimum, if not eliminated. The dynamic brake allows more flexible mechanical tolerances resulting in consistent up and down reg rod travel times.

Preparation for the modernization of the reactor instrumentation is continuing. For example, the electronics for the Ph monitoring of the Secondary Cooling system has been replaced by reliable modern equipment. Four new millivolt to current converters with RFI immunity have been installed to replace present temperature MV/I transmitters. One of the reactor level transmitters was replaced by a modern strain gauge type transmitter, also incorporating the RFI immunity feature.



## D. SERVICES PROGRAMS

### NEUTRON ACTIVATION ANALYSIS AT THE FOOD AND DRUG ADMINISTRATION

W. C. Cunningham and W. B. Stroube  
(U. S. Food and Drug Administration, Washington, DC)

The Food and Drug Administration maintains a neutron activation analysis (NAA) unit in the reactor building of the National Bureau of Standards (NBS). The NAA program at FDA includes analytical support for regulatory activities and special projects as well as applications research. During the past year several projects were conducted in FDA's NAA laboratory with emphases on quality assurance and radiochemistry programs. The laboratory also participated in an analysis program sponsored by the Nutrient Composition Laboratory of the USDA and the Chemistry and Biology Research Institute of Agriculture Canada who have developed some new biological reference materials.

Radiochemical work in progress includes both pre- and post-irradiation techniques which are being developed and applied to food analyses. Chelex-100 chelating resin is being used for pre-irradiation separations. This work compliments other work done in the Environmental and Elemental Contaminants Branch using an inductively coupled plasma spectrometer (ICP). For elements determinable by both techniques, NAA will be used as a confirmational technique in the Branch's QA exercises. For other elements NAA's results are complementary and now provide more complete characterizations. Post-irradiation separations are performed using inorganic chromatographic resins. Limits of detection are low enough using this technique for the toxic elements As, Cr, and Se to be detected in most of the foods analyzed. Detection limits for Cr and Se were lowered by a factor of five to seventy, depending on the food matrix. For As detection limits were lowered even more significantly, in some cases by more than three orders of magnitude. Improvements were noted also for Ag, Mo, and Sb. Work is continuing to improve recoveries for these elements.

The FDA NAA laboratory was invited to participate in the investigation of the proposed biological reference materials (BRM's) being developed by Agriculture Canada and the USDA. Our laboratory provided the instrumental neutron activation analysis (INAA) results that will be used to generate the reference concentrations. We analyzed eight subsamples from each of the proposed BRM's for twenty elements. Results are currently being combined with those from the other techniques so that they will be available when the BRM's are distributed.



## SERVICE PROGRAMS

### PREPARATION OF F-18 LABELED RADIOTRACERS USING NBS REACTOR-PRODUCED F-18

W. C. Eckelman, M. Channing, and J. Bennett  
(National Institutes of Health, Clinical Center, Bethesda, MD)

F-18 is produced by irradiating 0.4g enriched  ${}^6\text{Li}_2\text{CO}_3$  for 2 hours at  $1.1 \times 10^{14}$  n/cm<sup>2</sup>/sec. The quartz ampule is then returned to NIH for processing in a semiautomatic processing facility. The quartz ampule is cracked and  $\text{Li}_2\text{CO}_3$  is mixed with cation exchange resin in water. The aqueous solution is transferred to a round bottom flask containing base and carrier fluoride. The water is evaporated and acetonitrile is added. The acetonitrile is evaporated and the process is repeated twice again. The substrate is then added to the fluoride. To date, two substrates have been used: (1) methyl 4,6-O-benzylidene 2,3-cyclic sulfate-B-D-Mannopyranoside--a precursor to 2-fluoro-2-deoxy glucose, and (2) the 6-triflate derivative of naltrexone. Both are produced in 60% radiochemical yield. Animal experiments will begin in the next year to study the biochemistry.

### NEUTRON CAPTURE PROMPT- $\gamma$ ACTIVATION ANALYSIS

D. L. Anderson, G. E. Gordon, W. B. Walters, W. H. Zoller, and M. E. Kitto  
(University of Maryland, College Park, MD)

In the past year, over 800 samples of various types have been analyzed at the neutron capture prompt-gamma activation analysis (PGAA) facility at the National Bureau of Standards (NBS) reactor. Much of the research involved dealt with continuing studies of gas-phase species in the atmosphere, matrix effects encountered in PGAA, and the analysis of lumped burnable poisons. Several new studies, primarily of geochemical interest, were also initiated.

Although initially aimed toward the characterization of atmospheric boron, we have expanded one of our studies to encompass other elements, such as S, Cl (via PGAA) and Br, I and Se (using INAA). Using stacks of filters (described in last year's report), we have measured the particle and gas-phase contributions for these and several other elements in samples taken in Hawaii, Alaska, Wallops Island, College Park and Gaithersburg. The concentration of B trapped on particles, is of the order of 1 ng/m<sup>3</sup> in all the tropospheric samples taken, regardless of location. High altitude samples from Mauna Loa Observatory yield concentrations of less than ~0.2 ng/m<sup>3</sup> for both the particle and gas phases. Tropospheric gas-phase boron varied greatly (<0.1 to >100 ng/m<sup>3</sup>) from location to location and is believed to be largely due to oceanic and fossil-fuel sources. Data on the other elements are only

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preliminary. One interesting feature is that we observe gas-phase Se at levels 5 to 10 times lower than that reported by other groups. We believe our present gas-sampling method, designed to collect acidic gases, does not collect the Se in its atmospheric chemical form (e.g., elemental or organic). We are considering other approaches.

We noted last year that a potentially severe matrix effect is observed in PGAA for hydrogenous samples; the sensitivity (counts/sec·mg) for all elements measured so far increases with increasing H content. An in-depth study involving prepared standards is now underway to detail the variations for each important element and their causes in a beam-oriented system such as ours.

In a new geochemical project, in collaboration with Dr. Nathalie Valette-Silver of the Carnegie Institution of Washington, we are analyzing very interesting samples from deep ocean hydrothermal vent areas. The mounds of sulfide deposits formed (often referred to as "smokers" or "chimneys") contain relatively large amounts of the elements Cu, Zn, Fe, Au and Ag, among others. The deposits and related fluids are interesting not only because of the potential for understanding the formation of ore deposits, but also because of the implications for tectonic geochemistry in general. Other geologically-oriented projects include the measurement of Cd in shale oil and oil shale (with Battelle Pacific Northwest Laboratories) and the characterization of a new raw oil shale standard (with Dr. Michael D. Glascock of the University of Missouri).

Personnel from the Center for Analytical Chemistry have also made use of the PGAA setup in the past year in a number of projects described elsewhere in this document.

ATMOSPHERIC AND ENVIRONMENTAL STUDIES BY INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS

G. E. Gordon and W. H. Zoller  
(University of Maryland, College Park, MD)

We continue to make extensive use of instrumental neutron activation analysis (INAA) to determine concentrations of about 35 elements in samples of atmospheric particulate matter collected from ambient air (now mostly at remote sites such as Hawaii and rural sites in the continental U.S.) and in particles released from major sources such as volcanoes. By measuring concentrations of such a large number of elements, we are able to identify contributions from the sources to the atmospheric burden at ambient sampling sites. Examples of some of these studies are discussed briefly in the following sections.

1. Compositions of Atmospheric Particles at Mauna Loa Observatory, Hawaii

Until recently, there existed no long continuous record of concentrations of elements on particles at a site remote from local activities despite demonstration of the enormous value of the long-term CO<sub>2</sub> record (since 1957) at Mauna Loa Observatory (MLO) in Hawaii for observing CO<sub>2</sub> seasonal variations and long term increase. Fortunately, since mid-1979, the National Oceanic and Atmospheric Agency (NOAA) has supported weekly collections of filters at MLO and analysis of them by our group using INAA. Results of analysis of the MLO samples through 1982 were discussed in last year's progress report. Since January 1983, we have continued to collect samples on a weekly basis, but analysis of the samples was interrupted because of eruptions from Kilauea and Mauna Loa volcanoes off and on since that time. As discussed below, we have instead analyzed samples of the volcanic material. Recently, we have again begun to analyze MLO samples taken since January 1983.

Several papers based on this work have been submitted for publication and two have been published<sup>1,2</sup>.

2. Composition of Emissions from Volcanoes

In order to interpret the compositions of particles collected at MLO and other remote sites, we must know the compositions of particles released by various natural and anthropogenic sources. One potentially very important natural source is volcanic emissions, which have been heavily investigated by this group for several years. Last year's progress report described studies of four Central American volcanoes. This year we have focused attention on the Hawaiian volcanoes, Kilauea and Mauna Loa.

Kilauea erupted in January 1983 and has continued to erupt at various times since then. Emissions from the initial eruptive phase were inadvertently collected



at our MLO sampling station (see Section 1) and analyzed by INAA at the NBS reactor, revealing unusually large concentrations of Se, As, In, Au, and S, as expected for volcanic emissions. In a paper published in Science, Zoller et al. noted that strikingly large concentrations of Ir were also observed. As Ir enrichments have not previously been observed in volcanic emissions, the results suggested that Kilauea is part of an unusual volcanic system which may be fed by magmas from the earth's mantle. The Ir enrichment appears to be linked with the high F content of the volcanic gases, suggesting its release as  $\text{IrF}_6$ .

Previous workers<sup>4</sup> had observed huge Ir enrichments at the Cretaceous-Tertiary (K-T) boundary layer in sediments, which they suggest arose from the impact of a very large meteorite. The results obtained from Kilauea suggest that volcanic emissions of this type might provide an alternate explanation.

We have subsequently taken samples much closer to the volcano to obtain much greater masses of volcanic material and analyzed these samples at the NBS and Los Alamos reactors. The results confirm and extend the results obtained from the MLO samples. A paper concerning these results is nearly ready for submission.

Mauna Loa volcano began erupting on 24 March 1984. Members of our group began collecting samples on 27 March and continued sampling, both with airplanes and on the ground until 15 April. The samples are being analyzed by INAA at the NBS and Los Alamos Reactors.

### 3. South Pole Aerosol

As a part of the study of particles in global circulation, particles have been collected from the very pristine atmosphere of the South Pole since 1971 (e.g. Ref. 5). During the past year, G. Tuncel has analyzed most of the samples collected there since 1977. Results for some of the elements observed are summarized in Table 1.

Most of the analyses of the South Pole samples are being done by INAA, which involves only the taking of  $\gamma$ -ray spectra with Ge(Li) detectors after the irradiations. However chemical separations are being used on some South Pole samples in order to observe Ir, which is present in extremely small concentrations, typically  $10^{-4}$  pg/m<sup>3</sup> of air. On the basis of concentrations of several metals at the South Pole, Cunningham and Zoller<sup>5</sup> estimated the total influx of meteoritic material to the earth's atmosphere. However, Ir is a much more sensitive indicator of meteoritic material than most other metals. Preliminary results from the Ir analyses suggest that the influx of meteoritic material is much smaller than indicated by most experts in the field.



#### 4. Arctic Haze

During the winter and spring of each year, the Arctic atmosphere contains high concentrations of aerosol, which is largely pollution-derived. This Arctic haze is observed over the entire Arctic basin and tends to appear in distinct layers or "haze bands" which are typically several hundred to several thousand feet thick. Much of the material is thought to have its source in Asia.

To gain a better understanding of the Arctic haze, P. Sheridan joined an aircraft experiment organized by NOAA specifically for study of the problem. He collected particles from several flights taken in March and April, 1983. In order to relate his results to the rest of the work being done on particles by this group, he has analyzed the bulk filter samples by INAA for about 35 elements. Some very lightly loaded samples were also collected on transmission electron microscope (TEM) grids for study of the individual particle characteristics by a variety of microscopic techniques, especially the analytical electron microscope (AEM) and the laser microprobe mass analyzer (LAMMA). The latter studies are being conducted in the Gas and Particulate Science Division of the Center for Analytical Chemistry of the NBS, where Mr. Sheridan is employed while also being a graduate student at the University of Maryland.

#### 5. Composition of Particles from Polluted Cities

The Asia dust transported to MLO in Hawaii in large amounts each spring (see Section 1 and Ref. 1) often has a composition quite unlike that of soils from other parts of the world (e.g. high concentration of As). We suspect that the dust, which originates from dust storms in China, picks up contaminants as it passes over the populated and industrial areas along the coast of China and in Korea and Japan. As a starting point in testing this hypothesis, we obtained fifteen air filter samples collected in Beijing, China by T. Novakov's group in Berkeley and previously analyzed by x-ray fluorescence (XRF) by them. D. Hermann and Ilhan Olmez subjected them to INAA to obtain data for additional elements. The INAA results are now being compared with the XRF data in preparation for interpretation of the combined data set.

#### 6. Size Distribution of Resuspended Particles Bearing Various Elements

Much of the suspended particulate matter in the atmosphere is wind-entrained soil. Because of the importance of this component, we need to know its composition rather well to interpret airborne particle compositions. C. M. Thompson designed and built a chamber for the re-suspension of dried, sieved, soil samples and collection of separate size fractions of the particles. Soils from several areas have been resuspended, and the various size groups analyzed by INAA at the NBS reactor. The

soils under investigation were collected from MLO, two places in China, and in Laurel, MD.

#### 7. Composition of Particles Released by Wood Combustion

Wood combustion is an important source of atmospheric particles, both anthropogenic and natural (from forest fires, slash burning, etc.). Thus, it is important to characterize these particles in order to identify their contribution to ambient air. Frank Guenther made a sampling trip to Fairbanks, AK, from 7 to 15 February 1984, as that city has a major air pollution problem in winter due to residential wood and coal burning and motor vehicles. Air samples were taken at a downtown and a residential location, the latter having a history of severe pollution from wood-burning stoves, with complaints of visibility and respiratory problems. Samples were also taken from various wood stoves burning aspen, birch, and spruce wood, and of motor vehicle and coal-fired plant emissions in that area. The major interest in this study is in identifying organic compounds associated with these sources. That part of the study is being done in the Organic Analytical Research Division of the Center for Analytical Chemistry at NBS, where Mr. Guenther is an employee while also pursuing his graduate work at the University of Maryland. In order to relate his observations to the other studies we are doing, he is also analyzing many of the samples by INAA at the NBS reactor.

#### 8. Shenandoah Valley Samples

One of the major environmental problems of our time is acid deposition. To control acid deposition in an optimal way, we must identify the sources of acid precursors, find out how they are transported and deposited, and how they are chemically converted to acids. In work supported by EPA, we are trying to identify elements borne by atmospheric particles that can serve as characteristic signatures of certain types of sources or areas of the country. To do this, S. Tuncel and I. Olmez are subjecting samples collected by EPA to analysis by INAA. They collected samples for 15 months at rural sites in Kentucky, Indiana, and Ohio<sup>6</sup>, and for three weeks in the Shenandoah Valley<sup>7</sup>. They collected particles for two size fractions, greater and less than 2.5- $\mu$ m diameter and analyzed them by x-ray fluorescence (XRF). The XRF method is a rapid, highly automated technique for analyzing large numbers of samples, but it mainly observes major elements. INAA is more expensive and time-consuming than XRF, but it yields data for many trace elements that are potentially useful tracers, e.g., Se, As, Sb, and In. The combined XRF and INAA results yield data for about 40 elements. We are mainly analyzing fine particles, as they provide much more information about sources than large particles, which are dominated by

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Table 1. Summer and Winter Average Concentration for Some Elements at the South Pole

| Element | Conc. unit        | 1978      | 1979      | Concentration<br>1980 | 1981      | 1982      |
|---------|-------------------|-----------|-----------|-----------------------|-----------|-----------|
| Na      | ng/m <sup>3</sup> |           |           |                       |           |           |
| Summer  |                   | 12±9      | 6±4       | 1.9±1.2               | 5±2       | 13±10     |
| Winter  |                   | 30±28     | 28±41     | 3.1±2.5               | 31±50     | 32±24     |
| Mg      | ng/m <sup>3</sup> |           |           |                       |           |           |
| Summer  |                   | 1.7±0.8   | 1.4±0.7   | 0.8±0.6               | 1.1±0.5   | 1.9±2.2   |
| Winter  |                   | 3.5±1.9   | 4±6       | 2.5±1.4               | 3±5       | 3.8±2.5   |
| Cl      | ng/m <sup>3</sup> |           |           |                       |           |           |
| Summer  |                   | 7±9       | 4±6       | 3±5                   | 10±13     | 7±13      |
| Winter  |                   | 40±34     | 45±70     | 14±17                 | 41±48     | 36±25     |
| Al      | ng/m <sup>3</sup> |           |           |                       |           |           |
| Summer  |                   | 1.7±2.1   | 0.46±0.3  | 0.8±0.6               | 1.3±0.6   | 0.8±0.5   |
| Winter  |                   | 2.8±2.8   | 0.37±0.5  | 0.2±0.1               | 0.3±0.2   | 0.2±0.1   |
| Sc      | mg/m <sup>3</sup> |           |           |                       |           |           |
| Summer  |                   | 0.37±0.3  | 0.07±0.05 | 0.07±0.05             | 0.26±0.13 | 0.11±0.08 |
| Winter  |                   | 1.8±4     | 0.03±0.01 | 0.03±0.06             | 0.14±0.2  | 0.02±0.06 |
| Mn      | ng/m <sup>3</sup> |           |           |                       |           |           |
| Summer  |                   | 12±8      | 5.5±3     | 7±5                   | 65±79     | 10±4      |
| Winter  |                   | 9±6       | 1.1±0.9   | 5.2±0.5               | 5±5       | 3.9±2.4   |
| Fe      | ng/m <sup>3</sup> |           |           |                       |           |           |
| Summer  |                   | 0.76±0.75 | 0.38±0.25 | 0.36±0.3              | 5.2±0.6   | 0.92±0.6  |
| Winter  |                   | 1.1±0.33  | 0.07±0.06 | 0.32±0.2              | 0.28±0.3  | 0.23±0.19 |
| S       | ng/m <sup>3</sup> |           |           |                       |           |           |
| Summer  |                   | 71±45     | 64±47     | 61±37                 | 99±60     | 64±19     |
| Winter  |                   | 34±9      | 39±11     | 28±19                 | 28±19     | -         |
| As      | pg/m <sup>3</sup> |           |           |                       |           |           |
| Summer  |                   | 2.5±1.8   | 3±2       | 3±3                   | 19±23     | 4.6±2.5   |
| Winter  |                   | 1.9±1.4   | 1.4±0.6   | 1.3±1.4               | 2.2±1.4   | 2.0±1.1   |
| Se      | pg/m <sup>3</sup> |           |           |                       |           |           |
| Summer  |                   | 7±4       | 8±4       | 8±6                   | 18±16     | 8±3       |
| Winter  |                   | 5±2       | 4±0.9     | 3±2                   | 4.5±2     | 4.3±3     |
| Br      | ng/m <sup>3</sup> |           |           |                       |           |           |
| Summer  |                   | 0.12±0.08 | 0.16±0.16 | 0.07±0.05             | 1.1±1.3   | 0.17±0.08 |
| Winter  |                   | 0.05±0.02 | 0.08±0.03 | 0.04±0.03             | 0.06±0.06 | 0.07±0.06 |
| Sb      | pg/m <sup>3</sup> |           |           |                       |           |           |
| Summer  |                   | 3±3       | 1.4±1.1   | 2.8±1.9               | 3.8±3     | 4.0±2.9   |
| Winter  |                   | 0.69±0.32 | 2.0±2.1   | 1.1±1.0               | 0.9±0.9   | 1.4±1.8   |
| I       | ng/m <sup>3</sup> |           |           |                       |           |           |
| Summer  |                   | 0.37±0.5  | 0.17±0.15 | 0.19±0.13             | 0.19±0.13 | 0.15±0.1  |
| Winter  |                   | 0.11±0.09 | 0.11±0.08 | 0.06±0.03             | 0.15±0.17 | 0.08±0.08 |

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Table 2. Average Concentrations and Standard Deviations of Elements and Species Observed in Fine Fractions of Shenandoah Samples

| Species                       | Anal. Method <sup>a</sup> | No. spls. detected | Concentration (ng/m <sup>3</sup> ) |                                   |
|-------------------------------|---------------------------|--------------------|------------------------------------|-----------------------------------|
|                               |                           |                    | Arithmetic, $\bar{x} \pm \sigma$   | Geometric, $\bar{x}_g (\sigma_g)$ |
| Na                            | INAA                      | 33                 | 51±27                              | 46 (1.6)                          |
| Al                            | INAA                      | 32                 | 42±28                              | 28 (2.4)                          |
| Si                            | XRF                       | 32                 | 133±160                            | 87 (2.4)                          |
| S                             | XRF                       | 32                 | 4400±3300                          | 3300 (2.2)                        |
| Cl                            | INAA                      | 33                 | 13±14                              | 8.6 (2.4)                         |
| K                             | INAA                      | 32                 | 66±32                              | 59 (1.7)                          |
| Ca                            | INAA                      | 32                 | 37±26                              | 31 (1.9)                          |
| Sc                            | INAA                      | 30                 | 0.012±0.015                        | 0.0080 (2.5)                      |
| V                             | INAA                      | 32                 | 1.25±1.01                          | 0.97 (2.0)                        |
| Cr                            | INAA                      | 30                 | 0.6±0.6                            | 0.40 (2.6)                        |
| Mn                            | INAA                      | 31                 | 2.5±1.8                            | 2.0 (2.0)                         |
| Fe                            | INAA                      | 31                 | 53±58                              | 43 (1.9)                          |
| Co                            | INAA                      | 32                 | 0.06±0.07                          | 0.047 (2.0)                       |
| Cu                            | INAA                      | 24                 | 6.4±4.4                            | 5.2 (2.0)                         |
| Zn                            | INAA                      | 32                 | 9±7                                | 7.4 (1.9)                         |
| As                            | INAA                      | 30                 | 0.40±0.31                          | 0.27 (2.6)                        |
| Se                            | INAA                      | 32                 | 1.3±0.94                           | 1.05 (2.0)                        |
| Br                            | XRF                       | 33                 | 7.5±2.3                            | 7.0 (1.5)                         |
| Cd                            | INAA                      | 24                 | 2.4±7.4                            | 0.93 (2.6)                        |
| Sb                            | INAA                      | 32                 | 0.30±0.14                          | 0.26 (1.8)                        |
| I                             | INAA                      | 21                 | 0.48±0.30                          | 0.43 (1.6)                        |
| Cs                            | INAA                      | 21                 | 0.028±0.021                        | 0.022 (2.0)                       |
| La                            | INAA                      | 27                 | 0.09±0.09                          | 0.056 (3.6)                       |
| Ce                            | INAA                      | 32                 | 0.23±0.21                          | 0.18 (2.1)                        |
| Sm                            | INAA                      | 25                 | 0.008±0.005                        | 0.0063 (2.1)                      |
| W                             | INAA                      | 19                 | 0.06±0.04                          | 0.045 (2.0)                       |
| Pb                            | XRF                       | 32                 | 51±18                              | 47 (1.5)                          |
| Th                            | INAA                      | 17                 | 0.024±0.031                        | 0.014 (2.6)                       |
| SO <sub>4</sub> <sup>2-</sup> | IC                        | 28                 | 13,600±10,100                      | 10,500 (2.1)                      |
| NO <sub>3</sub> <sup>-</sup>  | IC                        | 15                 | 600±1100                           | 340 (2.5)                         |
| H <sup>+</sup>                | Chem.                     | 26                 | 96±128                             | 40 (4.4)                          |
| C (total)                     | Chem.                     | 25                 | 1750±970                           | 1420 (2.1)                        |
| C (org.)                      | Chem.                     | 21                 | 540±460                            | 375 (2.4)                         |
| C (elem.)                     | Chem.                     | 25                 | 1300±760                           | 990 (2.4)                         |
| NH <sub>4</sub> <sup>+</sup>  | IC                        | 26                 | 3400±2000                          | 2900 (1.8)                        |
| N (total)                     | Chem.                     | 26                 | 1270±730                           | 1100 (1.7)                        |
| Mass                          | β                         | 32                 | 42,000±29,000                      | 33,000 (2.1)                      |

<sup>a</sup>XRF = x-ray fluorescence; INAA = instrumental neutron activation analysis; IC = ion chromatography; Chem. = other chemical methods; β = beta gauge.



local soil. Back-trajectories for air masses sampled during each period were calculated by J. Parrington using a model and meteorological data from NOAA to identify the areas over which the air was transported in order to see if the compositions of particles from different areas have characteristic signatures. The INAA measurements have been done on all 33 Shenandoah samples, with the results shown in Table 2. This work has been submitted for publication in Environmental Science Technology.

Over 200 fine-fraction samples have been selected from the 1400 collected in the Ohio River Valley Study (KY, IN, OH sites). Most of these have been analyzed by INAA for short-lived activities and are now being irradiated to observe long-lived species.

#### 9. Philadelphia Samples

During the summer of 1982, EPA sponsored detailed studies of the sources of atmospheric particles in the atmosphere of Philadelphia. Particles were collected at three ambient sampling sites in that area for one month using dichotomous samplers, which collect particles with diameters above and below 2.5  $\mu\text{m}$  separately. EPA personnel analyzed all of the samples by XRF and sent the fine fractions here for their analysis by INAA. I. Olmez and A. Sheffield analyzed these samples and have submitted the results to EPA. We are not reporting the results here, as EPA may use the combined data sets in a "blind", round-robin test of receptor models used for various research groups. Samples were also collected from seven important sources of particles in the Philadelphia area: a coal-fired power plant, two oil-fired plants, a refinery, an incinerator, an Al plant, and an Sb roaster. They were first subjected to XRF<sup>8</sup>, and then sent here for INAA. Three sets of fine and coarse samples from each source were analyzed by Olmez and Sheffield, and the results are being prepared for publication.

#### 10. Deep Creek Lake Samples

During the summer of 1983, EPA, DoE, and EPRI and their contractors collected ambient samples at a site near Deep Creek Lake, MD and in stacks and plumes of several coal-fired plants upwind of the site. These samples have been subjected to XRF in other laboratories and will be analyzed by INAA by our group. We have received the ambient samples and A. Sheffield has begun the analysis of them.

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1. J. R. Parrington, W. H. Zoller, and N. K. Aras, Asia Dust: Seasonal Transport to the Hawaiian Islands, Science 220, 195 (1983).

## A COMPTON PROFILE EXPERIMENT IN GRAPHITE

L. M. Pecora and A. C. Ehrlich  
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We report here on the use of the Compton effect to study the momentum density of graphite. When a gamma ray scatters off an electron the wavelength of the gamma ray changes. This measureable change is a function of the angle of scatter and the value of the electron's momentum along the direction of the scattering vector (see Figure 1). By measuring the number of gamma rays scattered by the electrons of a solid at a particular fixed angle as a function of wavelength (energy) one gets a measure of the relative probability of finding an electron in the solid being studied as a function of the component of the electron's momentum along the scattering vector. This relative probability is related to the probability of an electron having a certain vector value for its momentum. This latter probability is called the momentum density. The data gathered on the momentum density in a Compton scattering experiment of this nature is called the Compton profile.

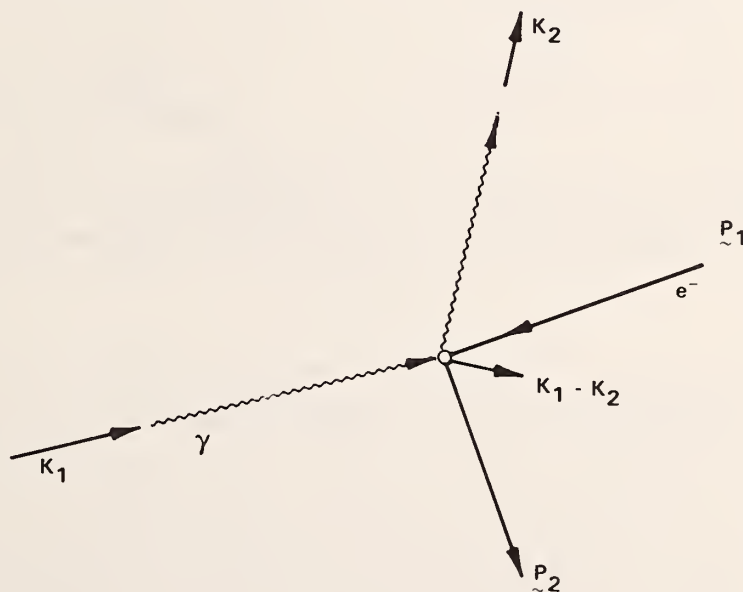


Figure 1. Diagram of the Compton scattering of a gamma ray from an electron with a particular initial value of momentum  $p_1$ . The gamma ray has initial momentum  $k_1$  and final momentum  $k_2$ . The scattering vector is the difference  $k_1 - k_2$  and the projection of  $p_1$  along the scattering vector is the component of  $p_1$  which is resolved in the detection of the scattered  $\gamma$ -ray.

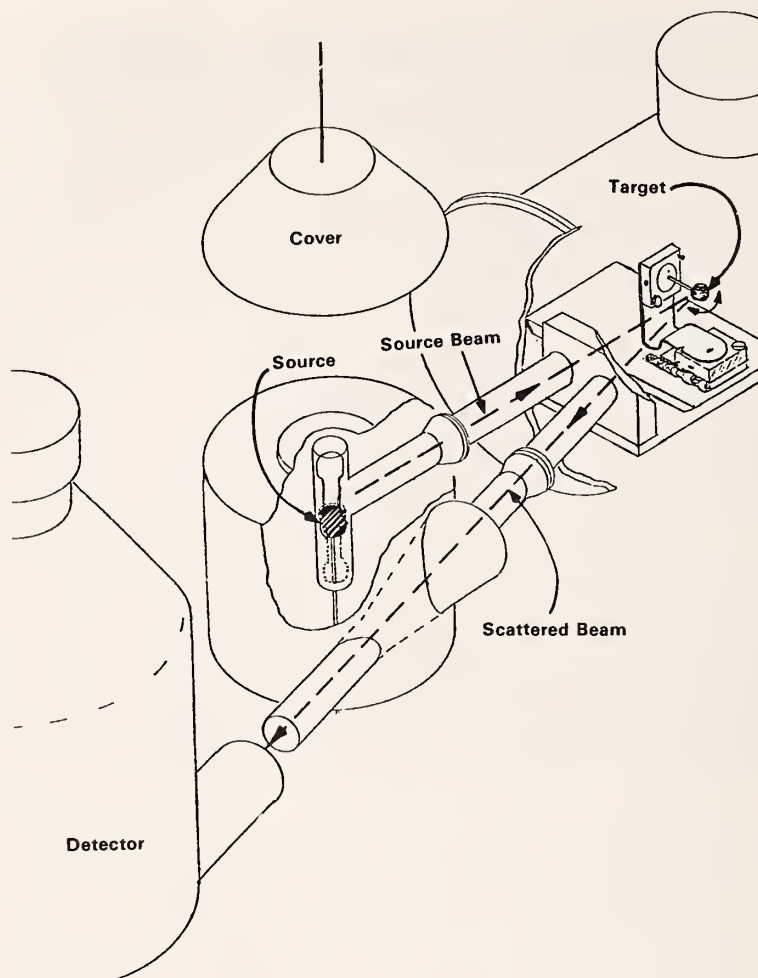


Figure 2. Diagram of the experimental apparatus showing the source container, source beam tube, target (graphite in this case), the scattered beam tube and the detector.

Compton profiles taken for various orientations of a single crystal sample are particularly useful for inferring the structure of the 3 dimensional momentum density of the electrons in the particular material being studied. The momentum density itself relates directly to various physical quantities which are of great interest: the Fermi surface, the band structure (energy states), and the structure of the electron wave functions.

We have constructed an experimental apparatus for measuring Compton profiles of various materials using gamma radiation from an Au-foil source which has been irradiated in the National Bureau of Standards Reactor so that Au(198) is present in the source (see Figure 2). The source is transported to the High Radiation Laboratory at the Naval Research Laboratory and placed in the lead source container

so as to emit a collimated beam of gamma rays consisting primarily of 412 keV photons. The sample whose electrons scatter the gamma rays is held in a specially made sample holder which allows rotation of the sample about two axes. The apparatus is shielded in such a way that the only gamma rays detected are those scattered at a  $170^\circ$  angle. The detection is accomplished by a germanium detector. The resolution of the detector counts into energy channels is done by a multi-channel analyzer. The analyzer is interfaced with a computer to facilitate the transfer of the data and the data analysis.

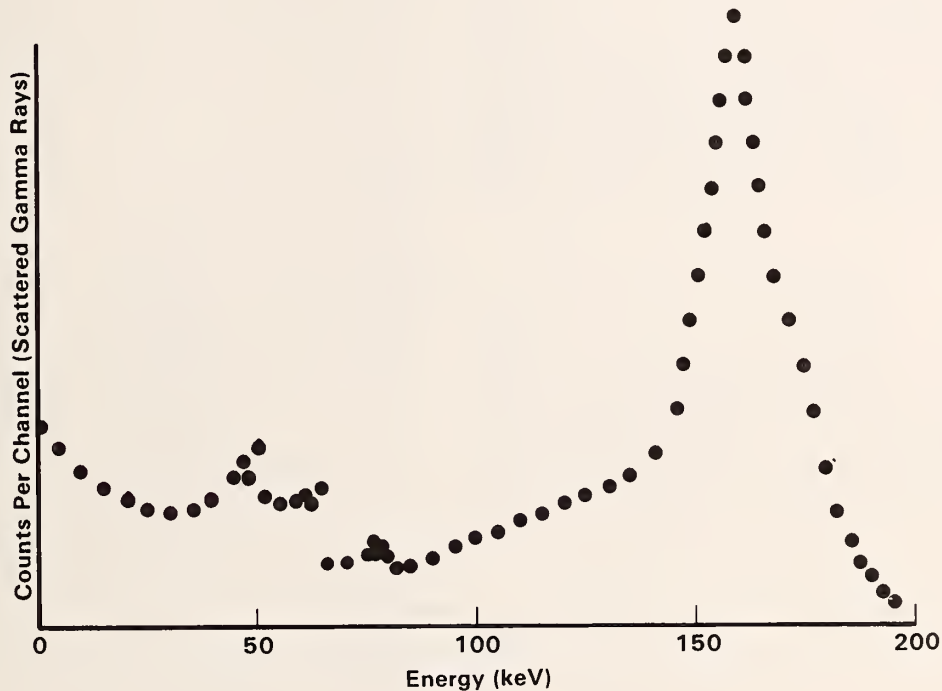


Figure 3. Plot of the number of gamma rays detected as a function of energy (channel) in a preliminary Compton profile experiment.

Figure 3 shows the first data taken with this apparatus. The target material was highly ordered pyrolytic graphite. The orientation was such that the graphite  $c$ -axis was parallel to the source beam. The main peak in the plot results from the Compton scattering of 412 keV radiation from the electrons of the graphite. The central part of the peak is due to the scattering from the conduction band electrons and the nearby broader parts of the main peak are due to the scattering of the gamma rays from the core electrons of the graphite. The smaller peaks at lower energies result from the Compton scattering of lower energy gamma rays emitted from the Au source.



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At this point we are working to eliminate more background radiation from the experimental set-up. We are also working on software for the analysis of the Compton files, in particular the extraction of information on the momentum density from the data. Future experiments will include measurements of the Compton profiles of highly ordered pyrolytic graphite in various orientations.

# E. PERSONNEL ROSTER

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July 1984

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| U.S. DEPT. OF COMM.<br><b>BIBLIOGRAPHIC DATA SHEET</b> (See instructions)                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            | 1. PUBLICATION OR REPORT NO.<br>NBS/TN-1207 | 2. Performing Organ. Report No. | 3. Publication Date<br>February 1985                             |
| 4. TITLE AND SUBTITLE<br><br>NBS Reactor: Summary of Activities July 1983 to June 1984                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                                             |                                 |                                                                  |
| 5. AUTHOR(S)<br>F. J. Shorten, Ed.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |                                             |                                 |                                                                  |
| 6. PERFORMING ORGANIZATION (If joint or other than NBS, see instructions)<br><br>NATIONAL BUREAU OF STANDARDS<br>DEPARTMENT OF COMMERCE<br>WASHINGTON, D.C. 20234                                                                                                                                                                                                                                                                                                                                                                                                                                                    |                                             | 7. Contract/Grant No.           | 8. Type of Report & Period Covered<br><br>July 1983 to June 1984 |
| 9. SPONSORING ORGANIZATION NAME AND COMPLETE ADDRESS (Street, City, State, ZIP)                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |                                             |                                 |                                                                  |
| 10. SUPPLEMENTARY NOTES<br><br><input type="checkbox"/> Document describes a computer program; SF-185, FIPS Software Summary, is attached.                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |                                             |                                 |                                                                  |
| 11. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)<br><br>This report summarizes all those programs which depend on the NBS reactor. It covers the period from July 1983 through June 1984. The programs range from the use of neutron beams to study the structure and dynamics of materials through nuclear physics and neutron standards to sample irradiations for activation analysis, isotope production, radiation effects studies, neutron radiography, and nondestructive evaluation. |                                             |                                 |                                                                  |
| 12. KEY WORDS (Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)<br>Activation analysis; crystal structure; diffraction; isotopes; molecular dynamics; neutron; neutron radiography; nondestructive evaluation; nuclear reactor; radiation                                                                                                                                                                                                                                                                                                              |                                             |                                 |                                                                  |
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